

GEORGIA INSTITUTE OF TECHNOLOGY  
OFFICE OF RESEARCH ADMINISTRATION  
RESEARCH PROJECT INITIATION

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Date: March 17, 1975

Project Title: Effects of High Pressure and Inhibitors on 'Metal Dusting'  
Corrosion Pertinent to Coal Gasification Systems

Project No: E-19-635

Principal Investigator: Dr. R. F. Hochman

Sponsor: U. S. Bureau of Mines

Agreement Period: From 3/1/75 Until 2/29/76

Type Agreement: Grant No. G0155088

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Semi-Annual Technical Report, Annual/Final Technical  
Report

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Assigned to: Chemical Engineering

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GEORGIA INSTITUTE OF TECHNOLOGY  
OFFICE OF CONTRACT ADMINISTRATION  
SPONSORED PROJECT TERMINATION

Date: 8/1/77

Project Title: Effects of High Pressure and Inhibitors on Metal Dusting Corrosion  
Pertinent to Coal Gasification Systems.

Project No: E-19-635

Project Director: Dr. R. F. Hochman

Sponsor: U. S. Bureau of Mines

Effective Termination Date: 9/30/76

Clearance of Accounting Charges: 9/30/76

Grant/Contract Closeout Actions Remaining:

- Final Invoice and Closing Documents
- Final Fiscal Report
- Final Report of Inventions
- Govt. Property Inventory & Related Certificate
- Classified Material Certificate
- Other \_\_\_\_\_

Assigned to: Chemical Engineering (School/Laboratory)

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GEORGIA INSTITUTE OF TECHNOLOGY  
ATLANTA, GEORGIA 30332

SCHOOL OF  
CHEMICAL ENGINEERING

June 13, 1975

Division of Metallurgy  
Bureau of Mines  
U.S. Department of the Interior  
18th and E Streets, N.W., Rm. 3522  
Washington, D. C. 20240

Attention: Mr. H. W. Leavenworth  
(COR) Technical Project Officer

Subject: Research Grant No. G0155088 entitled, "Effects of High Pressure and Inhibitors on 'Metal Dusting' Corrosion Pertinent to Coal Gasification Systems

Since initiating the project, work has been mainly confined to setting up equipment in our special, high-safety explosion laboratory, testing out equipment, and procurement of parts and materials. Delay has been experienced in the delivery of special high-pressure gas regulators and high-purity carbon monoxide. However, significant progress has been made in this first quarter.

A special corrosion-resistant atmospheric pressure reactor was designed and constructed for evaluating the effect of inhibitors on metal dusting corrosion. This reactor consists basically of a quartz tube with Vycor fittings welded to each end. Pyrex headers are vacuum sealed to these fittings for in- and outlet of the gases. A small diameter quartz thermocouple sheath welded to one of these headers extends to the center of the reaction tube, so that a thermocouple placed in the sheath can sense the temperature of the sample. A schematic diagram of the unit, including a list of notes and comments is attached.

A high-pressure high-temperature reactor was developed in cooperation with the Parr Instrument Company. It is anticipated that with this reactor we will be able to carry out the gas-metal reactions over the entire pressure range and entire temperature range proposed (pressures to 100 atmospheres and temperatures to 1500<sup>0</sup>F.) The reactor has also been designed to avoid catastrophic corrosive attack on the pressure system. Therefore, it should speed up our investigations, since it has made unnecessary the design and construction of the preliminary non-corrosion-resistant high pressure reactor. It was originally thought that such a step-wise approach would be necessary.

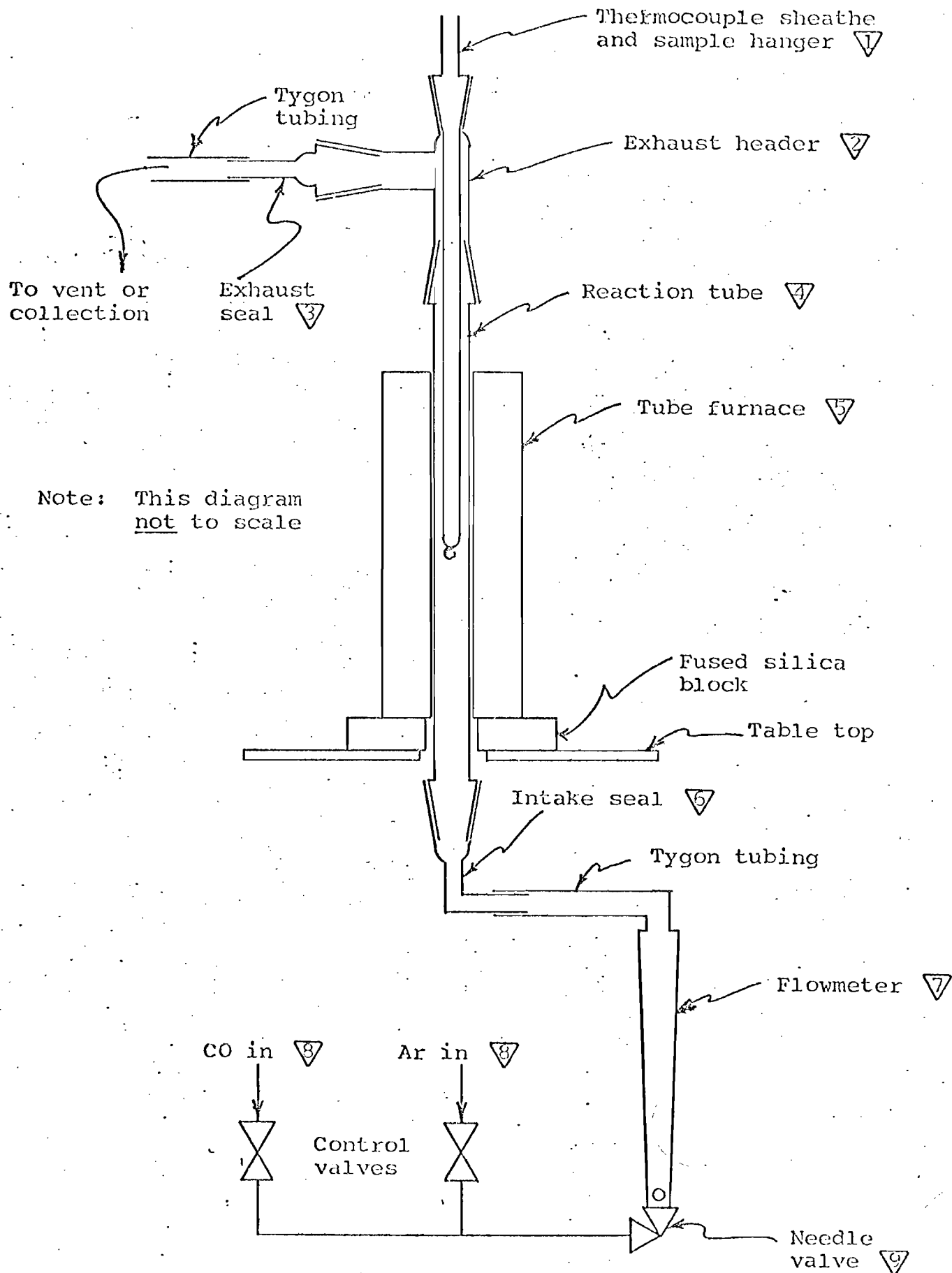
The reactor developed is presently being custom built by the Parr Instrument Company with delivery promised before the end of this month (June '75). The reactor will consist of a 500 ml cylindrical autoclave with a small internal furnace. The head and outer cylinder of the autoclave will be constructed of Monel 400. There will be Mullite insulation between the outer walls of the autoclave and the internal furnace to keep temperatures of the outer walls at a minimum. Water cooling of the outside surface of the autoclave can be applied when necessary. The internal furnace will have a cylindrical reaction chamber which is 1.250 in. in diameter and 4 in. high. The reaction gas will be fed through the head of the autoclave, impinge on the sample in the reaction chamber, and exit at the bottom through a valve. In addition to the gas line, two electrodes for the heating elements of the furnace and two thermocouples will be fed through the head of the autoclave. The electrodes will have high-temperature lava sealants, stainless steel bodies and a special high nickel alloy electrode core. This alloy is one commonly used for spark plugs. The thermocouples will be chromel-alumel, and the thermocouple protective sheaths will be made of Hastalloy C. The mounting fittings

on top of the autoclave for the thermocouples will also have stainless steel bodies. One thermocouple will reach into the reaction chamber, and the second one will sense the temperature at the autoclave outer wall. The autoclave will be further equipped with a Gage Block Assembly with a pressure gage to measure the internal gas pressure. The inside surfaces of the autoclave outer walls will be gold plated for corrosion resistance.

Only one graduate student was available to initiate research on this project during this start-up quarter. However, we have commitments of two graduate students for the next quarter. As it now stands, a post doctoral candidate and an undergraduate student are also involved in the research so that progress should accelerate.

Respectfully submitted,

~~Robert F. Hochman~~  
Project Director



See next page for notes and comments.

SCHEMATIC DIAGRAM OF THE ATMOSPHERIC REACTOR

NOTES:

- ▽1 Quartz tubing with Vycor fitting.
- ▽2 Pyrex, all fittings are ground glass.
- ▽3 Pyrex.
- ▽4 Quartz tube with Vycor fittings.
- ▽5 Lindberg Hevi-duty single zone tube furnace, type 54031A. Not shown is a Lindberg Hevi-duty digital controller, type 59344.
- ▽6 Pyrex.
- ▽7 Rotometer type. Air Products and Chemicals no. 09-1011.
- ▽8 Gas is taken from high pressure cylinders by means of a regulator and taken to the control valves in copper tubing.
- ▽9 This valve controls flow rate.

COMMENTS:

1. Another piece of equipment that is not shown is the ring stand that holds up the reaction tube during the cooling cycle of a test run.
2. At times it will be necessary to collect gas samples for analysis. This will be done using the same exhaust seal and tubing as in venting. The gas will simply be collected through water into a volumetric flask or sample bottle.
3. At such time as gas mixtures are evaluated, the gas intake control valves and flowmeters will have to be altered or replaced by a new system.

GEORGIA INSTITUTE OF TECHNOLOGY  
ATLANTA, GEORGIA 30332

SCHOOL OF  
CHEMICAL ENGINEERING

September 19, 1975

Mr. G. A. Young  
Contract Officer  
U. S. Dept. of Interior  
Bureau of Mines  
Branch of Contracts & Grants  
18th & E Sts., N.W. Room 2759  
Washington, D.C. 20240

Subject: Quarterly Financial Reports 1 and 2--Research Grant No. G0155088 -  
"Effects of High Pressure and Inhibitors on 'Metal Dusting' Corrosion  
Pertinent to Coal Gasification Systems"

Dear Mr. Young:

No personal services for the principle investigators have been charged to this Bureau of Mines research project during the first two quarters because of internal paper work necessary here at Georgia Tech. The charges are in a "holding" account at present. These charges will be transferred to the Bureau of Mines account by an internal budget amendment procedure which is being prepared at this time.

The balance in each category as of August 31, 1975, without the above mentioned charges was:

CATEGORY	ORIGINAL BUDGET	EXPENDED	BALANCE
Personal Services	\$25,100.00	\$2,078.00	\$23,022.00
Fringe Benefits	1,570.00	.00	1,570.00
Materials and Supplies	2,400.00	1,534.46	458.49
Equipment	1,600.00	407.05 encumbered	
Travel	500.00	1,573.00	27.00
Overhead	16,315.00	250.00 encumbered	250.00
TOTAL	\$47,485.00	1,308.63	15,006.37
		\$4,921.09 encumbered	\$40,333.86
		2,230.05	

Respectfully submitted,

Robert F. Hochman  
Project Director



GEORGIA INSTITUTE OF TECHNOLOGY  
ATLANTA, GEORGIA 30332

SCHOOL OF  
CHEMICAL ENGINEERING

September 15, 1975

Mr. C. B. Kenaham  
U.S. Department of Interior  
College Park, Metallurgy  
Research Center  
College Park, Maryland 20740

Attention: (COR) Technical Project Officer

Subject: 2nd Quarterly Technical Letter Report - Research Grant No. G0155088  
entitled, "Effects of High Pressure and Inhibitors on 'Metal Dusting'  
Corrosion Pertinent to Coal Gasification Systems

During the past three months, shakedown and preliminary runs of the atmospheric reactor were conducted. This was followed by the beginning of the pure metal-gas reaction studies. In the area of inhibitors, work has been performed to improve the methods of approach for this portion of the research. During this quarter the high pressure reactor was received and has been assembled for shakedown and metal-gas reaction studies.

The preliminary runs for the atmospheric reactor were in two separate areas. The first was a study of the reaction of 316 SS with C.P. grade CO (99.3% pure). These tests were conducted at a constant flow rate of approximately 40 cc/min. Despite some inaccuracies in the data, a curve of the expected shape for reactivity vs. temperature was obtained, and invaluable experience was gained on the part of the graduate students involved.

Following the preliminary studies a program to determine the optimum flow rate for the reactor was initiated. Data indicated a straight line dependence of

the reaction rate on the flow rate. A line was drawn based on reactivity vs. flow rate fitting the equation  $y = -1.091 \times 10^{-4} + 2.424 \times 10^{-5} x$ . It was found by means of a linear regression that the line was straight and significant at the 99.99 percentile level. For future runs, a flow rate must be arbitrarily chosen on the basis that it will give sufficient reaction and use a minimum of gas.

In the first of the pure metal-gas reaction studies, pure iron wire was reacted with Ultra High Purity CO (99.98% pure). The results of this series of runs were much more reproducible than those of previous tests. The data fit a smooth curve, despite what is felt as a lack of an efficient cleaning procedure as yet. The data is shifted very slightly to lower temperatures, and appears to indicate a higher reactivity than that reported by Westerman<sup>1</sup> although still in good experimental agreement. The greater reactivity can be explained by the method of sample exposure. Westerman used a sample boat which could lead to shielding a portion of the sample from the reacting gas. In this apparatus the sample is suspended directly in the reacting gas stream.

The high pressure system was received from the fabricator and assembled. A test stand has been set up in preparation for shakedown runs which will begin within a week. The initial runs will be made at 150 psig to determine the soundness of the test system and test procedures.

The inhibitor studies have been slowed by a problem resulting from the gas mixtures that are of initial interest cannot be legally mixed in conventional containers; therefore, alternate forms of containers are being considered and tested.

The continuation studies will be spent expanding the pure iron-carbon monoxide curve at atmospheric pressure, starting work in the high pressure region of pure iron-carbon monoxide reaction, and overcoming the problems in the inhibitor phase of the project. The majority of the startup problems inherent with new equipment and training new graduate students has been overcome and the generation of useful data can now proceed at a more efficient pace.

Bibliography:

1. Mechanism and Kinetics of Iron Deterioration in Carbon Monoxide, R. V. Westerman, doctoral thesis, directed by R. F. Hochman, Georgia Institute of Technology, December 1967, p. 64.

Respectfully submitted,

Robert F. Hochman  
Project Director

E-19-635

GEORGIA INSTITUTE OF TECHNOLOGY  
ATLANTA, GEORGIA 30332

SCHOOL OF  
CHEMICAL ENGINEERING

December 19, 1975

Mr. C. B. Kenaham  
U. S. Department of Interior  
College Park, Metallurgy Research Center  
College Park, Maryland 20740

ATTENTION: (COR) Technical Project Officer

SUBJECT: 3rd Quarterly Technical Letter Report--Research Grant No. G0155088,  
entitled, "Effects of High Pressure and Inhibitors on 'Metal  
Dusting' Corrosion Pertinent to Coal Gasification Systems.

Dear Mr. Kenaham:

Final shakedown runs of our high-pressure high-temperature reactor were conducted, followed by initial runs of iron in carbon monoxide at 10 and 20 atmospheres and 450°C. To make the reactor operational, a sophisticated new temperature controller had to be built. This improved temperature controller was essential to reduce temperature fluctuations. In the reactor, the control couple must also function as the sample couple because of space limitations and this caused difficulties in maintaining proper temperature control. The new controller, indicated a temperature control of  $\pm 1^\circ\text{C}$  in all ranges tested.

The wire of the heating element of the high-pressure high-temperature reactor was separately tested to determine if it would cause difficulties by metal dusting in the environments which it would experience in the reactor. A small sample of this heating wire was subjected to carbon bearing gases at about 700°C. It was found that after 20 hours of exposure, it had undergone no noticeable reaction either visibly or as measured by a microbalance. This was encouraging for heating element performance and durability is extremely important to the extensive studies planned.

During the past quarter, numerous 20-hour experimental runs were performed with the corrosion-resistant atmospheric-pressure reactor to check information on the reactivity of pure iron in pure carbon monoxide. It appears that for the 20-hour exposure any weight loss due to the loss of iron is nearly offset by a weight increase due to the gain of carbon due to diffusion into the surface, the formation of iron carbide, and tightly bonded graphite.

Because of this a pure iron sample was reacted for 6 days in pure carbon monoxide to see if extensive weight loss due to metal dusting could be brought

about by longer periods of exposure. This sample did indeed suffer a very measurable weight loss. After ultrasonic cleaning the weight loss was  $0.00247 \text{ gm/cm}^2$  compared to a before cleaning weight gain of  $0.0572 \text{ gm/cm}^2$ .

A second, additional, special corrosion-resistant atmospheric-pressure reactor and system, identical to the original system has also been built. This additional system will be used to conduct special metal-gas reactions while the original system is used for inhibitor studies. These studies are to be carried out to evaluate the prevention of metal dusting corrosion in coal gasification processes through inhibitors added to, or naturally occurring, in the gas.

The design and construction of the "inhibitor system" in conjunction with the corrosion-resistant atmospheric-pressure reactor to carry out the inhibitor studies was completed. However, the special gas regulator ordered for the inhibitor-containing gas mixtures has not been received as yet. Delivery of this special regulator has been delayed significantly by the manufacturer. However, when this part is received the complete system for the inhibitor studies should be operational. The inhibitor system does not affect the equipment configuration of the present reactor system, nor does it affect the experimental procedures at present except for the effective mixing of the gases.

Respectfully submitted,

Dr. Robert F. Hochman  
Project Director

E-19-635

GEORGIA INSTITUTE OF TECHNOLOGY  
ATLANTA, GEORGIA 30332

SCHOOL OF  
CHEMICAL ENGINEERING

March 10, 1976

Mr. C. B. Kenaham  
U.S. Department of Interior  
College Park, Metallurgy Research Center  
College Park, Maryland 20740

Attention: (COR) Technical Project Officer

Subject: 4th Quarterly Technical Letter Report-Research Grant No. G0155088,  
entitled, "Effects of High Pressure and Inhibitors on 'Metal  
Dusting' Corrosion Pertinent to Coal Gasification Systems."

During the past quarter, further runs with the high-pressure high-temperature reactor were made and pure iron was successfully and reproducibly reacted with pure carbon monoxide. The weight gain of the sample after 20 hours at 500°C and 20 atmospheres was about ten times as much as the weight gain at atmospheric pressure. The equipment has continued to function well with excellent control of temperature, pressure, gas flow, as well as efficient cooling of the outer walls of the reactor. For safety reasons we are cooling the outer walls of the reactor as much as possible. Therefore, as the temperatures and pressures are increased to 850°C and 100 atmospheres respectively, a more powerful heating element may be necessary. The heating element of the reactor is 300 watts at present, but additional heating capability can be obtained by increasing the voltage, therefore, lack of heating power should not be an immediate problem. Except for a more powerful heating element, no required modification of this high-pressure high-temperature reactor are now anticipated.

Several runs were made with the atmospheric-pressure reactor that functions in combination with the "inhibitor unit." These runs were followed by studies to determine the effect of trace amounts of hydrogen sulfide gas on the metal dusting of pure iron in pure carbon monoxide gas. To obtain the desired gas mixture, hydrogen sulfide gas was injected into the inhibitor unit by expanding a small, known volume of known pressure into a large evacuated holding tank. Carbon monoxide gas is then added to this tank to obtain the desired gas mixture at pressure of 1000 psi. The holding tank of the inhibitor unit is then used as the source of the gas mixture for the metal dusting experiments.

Eight 20-hour runs were made with pure iron being reacted with pure carbon monoxide containing 25 ppm hydrogen sulfide between 450° and 800°C. For comparison eight runs were made under identical conditions with only high purity carbon monoxide. The hydrogen sulfide reduced the metal dusting markedly as expected. With hydrogen sulfide the weight gain at the temperature of maximum reactivity was never more than 0.001 g/cm<sup>2</sup>; whereas without hydrogen sulfide, weight gain was 0.01 g/cm<sup>2</sup>. The results are shown in the attached figure.

Satisfactory shakedown runs were made with the second atmospheric-pressure reactor system. It is planned to use this system for both alloy and further inhibitor studies.

Thus, with three reactors in service, with all units functioning effectively significant data is now being obtained.

Respectfully submitted,

Robert F. Hochman  
Associate Director for Metallurgy  
Project Director

E-19-635

GEORGIA INSTITUTE OF TECHNOLOGY  
ATLANTA, GEORGIA 30332

SCHOOL OF  
CHEMICAL ENGINEERING

August 10, 1976

Mr. C. B. Kenaham  
U.S. Department of Interior  
College Park, Metallurgy Research Center  
College Park, Maryland 20740

Attention: (COR) Technical Project Officer

Subject: 5th Quarterly Technical Letter Report-Research Grant No. G0155088,  
entitled, "Effects of High Pressure and Inhibitors on 'Metal  
Dusting' Corrosion Pertinent to Coal Gasification Systems."

During the past quarter, further studies were completed with the high-pressure high-temperature reactor. These studies resulted in the evaluation of metal dusting corrosion of pure iron in pure carbon monoxide gas at 20 atmospheres pressure (300 psig) at temperatures of 450°, 500°, 550°, 600°, 650°, 700° and 750°C. Each sample of pure iron wire, 0.020 inch in diameter, was reacted for 20 hours. The experimental results are given in Table I. Weight gains as affected by temperature are plotted in Figure I. As may be seen in Figure I, the data points appear to give a curve that is similar in shape and location as those obtained at atmospheric pressure. However, metal dusting corrosion at 20 atmospheres pressure in the reactive temperature ranges was found to be to one thousand times greater than at atmospheric pressure! The "abnormality" of the 600°C data point was judged to be due to the rapid disintegration of the wire sample at this temperature and some of the products had fallen out of the hot zone before the full 20 hours reaction time had been



completed. Tests have been initiated to evaluate the attack as a function of time at 600°C and 20 atmospheres. This should give us a better understanding of the high-pressure reaction kinetics at this temperature.

The high-pressure high-temperature system was modified to produce and maintain the conditions required for further experimentation. The capacities of all power supply wiring, switches, and heating elements were increased to handle the power and maintain the control, anticipated for runs at high pressures.

At atmospheric pressure, additional runs were made in the corrosion-resistant atmospheric-pressure system to further evaluate the effects of low concentrations of hydrogen sulfide gas on the metal dusting corrosion of pure iron in carbon monoxide gas. Pure iron wire samples were evaluated for metal dusting corrosion in pure carbon monoxide gas containing 2.5, 5, 10, 25, 50, 100, or 500 ppm of hydrogen sulfide gas. Temperatures were about 450°, 500°, 550°, 600°, 650°, 700°, 750°, or 800°C. The experimental results are shown in Table II. The inhibiting effect of the hydrogen sulfide gas was observed at concentrations between 10 and 100 ppm. At 500 ppm no significant improvement was observed. Also, a rough design was prepared for a corrosion-resistant high-pressure, high temperature system for future evaluation of the effects of inhibitor gases on metal dusting.

Respectfully submitted,

/ Robert F. Hochman  
Associate Director for Metallurgy  
Project Director

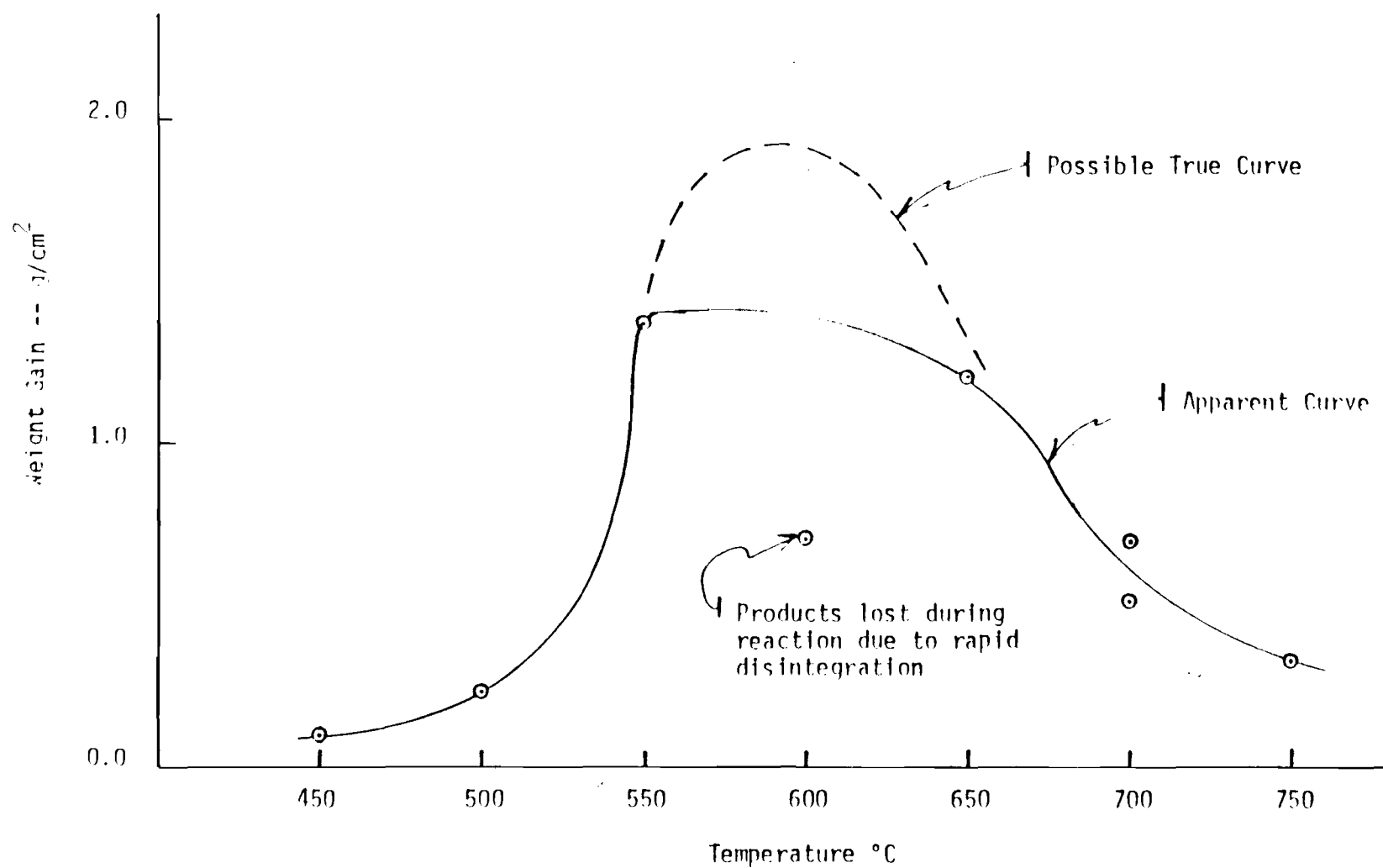


Figure I. Pure Iron Reacted with Pure CO(99.99%) at 20 Atmospheres.

TABLE I

Pure Iron Reacted with Ultra High  
Purity CO at 20 Atmospheres

<u>Temperature</u> (°C)	<u>Weight gain</u> (g/cm <sup>2</sup> )
450	$9.488 \times 10^{-2}$
500	$2.320 \times 10^{-1}$
550	1.369
600	$7.033 \times 10^{-1}$ *
650	1.205
700	$6.933 \times 10^{-1}$
700	$5.078 \times 10^{-1}$
750	$3.220 \times 10^{-1}$

\* Rapid disintegration of the sample at 600°C  
resulted in loss of products during reaction.

TABLE II

Effect of Hydrogen Sulfide on Reaction of Pure Iron  
With Ultra High Purity CO at Atmospheric Pressure

$H_2$ Content (ppm)	Temperature (°C)	Weight Gain (g/cm <sup>2</sup> )	$H_2S$ Content (ppm)	Temperature (°C)	Weight Gain (g/cm <sup>2</sup> )	$H_2S$ Content (ppm)	Temperature (°C)	Weight Gain (g/cm <sup>2</sup> )
2.5	466	$1.80 \times 10^{-4}$	25	465	$2.60 \times 10^{-4}$	500	457	$7.20 \times 10^{-4}$
	505	$1.62 \times 10^{-3}$		507	$1.20 \times 10^{-4}$		502	$1.76 \times 10^{-3}$
	561	$3.64 \times 10^{-3}$		562	$2.00 \times 10^{-4}$		556	$2.60 \times 10^{-3}$
	609	$3.38 \times 10^{-3}$		610	$2.20 \times 10^{-4}$		606	$2.96 \times 10^{-3}$
	665	$1.48 \times 10^{-3}$		663	$5.60 \times 10^{-4}$			
	710	$6.60 \times 10^{-4}$		703	$7.00 \times 10^{-4}$			
	756	$8.20 \times 10^{-4}$		753	$7.60 \times 10^{-4}$			
	802	$1.12 \times 10^{-3}$		801	$1.10 \times 10^{-3}$			
	854	$1.36 \times 10^{-3}$		456	$2.20 \times 10^{-4}$			
	458	$1.26 \times 10^{-3}$	50	501	$1.80 \times 10^{-4}$			
5	501	$1.02 \times 10^{-3}$		558	$2.60 \times 10^{-4}$			
	556	$7.00 \times 10^{-4}$		603	$3.20 \times 10^{-4}$			
	604	$2.60 \times 10^{-3}$		655	$6.20 \times 10^{-4}$			
	656	$1.88 \times 10^{-3}$		702	$4.80 \times 10^{-4}$			
	705	$7.00 \times 10^{-4}$		751	$7.80 \times 10^{-4}$			
	751	$1.14 \times 10^{-3}$		799	$1.08 \times 10^{-3}$			
	800	$1.40 \times 10^{-3}$		457	$2.60 \times 10^{-4}$			
	454	$4.00 \times 10^{-5}$	100	505	$4.80 \times 10^{-4}$			
	513	$4.00 \times 10^{-5}$		557	$5.40 \times 10^{-4}$			
	556	$4.00 \times 10^{-5}$		607	$5.80 \times 10^{-4}$			
10	607	$3.20 \times 10^{-4}$		659	$5.60 \times 10^{-4}$			
	658	$7.00 \times 10^{-4}$		707	$6.60 \times 10^{-4}$			
	708	$7.00 \times 10^{-4}$		756	$8.20 \times 10^{-4}$			
	755	$8.80 \times 10^{-4}$		803	$1.02 \times 10^{-3}$			

EFFECTS OF HIGH PRESSURE AND INHIBITORS ON  
METAL DUSTING CORROSION PERTINENT TO  
COAL GASIFICATION SYSTEMS

By

Robert F. Hochman  
Pieter Muije

SEMI-ANNUAL PROGRESS REPORT

Bureau of Mines Grant No. G0155088

September 15, 1975

GEORGIA INSTITUTE OF TECHNOLOGY  
Atlanta, Georgia

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EFFECTS OF HIGH PRESSURE AND INHIBITORS ON  
METAL DUSTING CORROSION PERTINENT TO  
COAL GASIFICATION SYSTEMS

By

Robert F. Hochman  
Pieter Muije  
Metallurgy Program

SEMI-ANNUAL PROGRESS REPORT

Bureau of Mines Grant No. G0155088

September 15, 1975

School of Chemical Engineering  
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Georgia Institute of Technology  
School of Chemical Engineering, Metallurgy Program  
Grant No. G0155088  
For Bureau of Mines, U.S. Department of the Interior

EFFECTS OF HIGH PRESSURE AND INHIBITORS ON  
METAL DUSTING CORROSION PERTINENT TO  
COAL GASIFICATION SYSTEMS

INTRODUCTION

The conditions of environment, material and temperature in many portions of coal gasification systems portend possible catastrophic deterioration of the metal or alloy by "metal dusting." Studies of this type of deterioration have been carried out over the past fifteen years. However, two areas which are of considerable importance for materials in coal gasification systems have received only limited study. Therefore, a two-phase systematic research program was initiated on March 1, 1975, addressed to these two areas: (1) the effects of pressure on metal dusting and (2) the prevention of this type of deterioration in coal gasification processes through inhibitors added to the gas.

The work reported herein covers the first six months of this program, which is being sponsored by the Division of Metallurgy of the Bureau of Mines, U.S. Department of the Interior under Research Grant No. G0155088.

BACKGROUND

"Metal dusting" is a form of catastrophic deterioration of metals in carbonaceous gases at elevated temperatures below the normal carburization range for these materials. The gases are normally reducing and contain one or more of the following: CO, CO<sub>2</sub>, Hydro-carbons, and often H<sub>2</sub>O and H<sub>2</sub>. The materials most commonly attacked are iron, nickel, cobalt, chromium and their alloys. Failures have occurred in a broad range of petroleum and petrochemical reactors, i.e., dehydrogenation units,

fired heaters, cracking units, etc. The same type of deterioration has also been found in the steel industry, in so-called "iron spots" in refractory bricks<sup>(1)</sup>; internal combustion engines, boilers and in certain nuclear reactors in the presence of CO. The varied nature of metal dusting is exemplified by the fact that no real definition of the attack could be made until recently, and this is still a very generalized definition involving a number of factors found in the typical deterioration attack. These are:

1. Environment--Gas phase; potentially carburizing and reducing with or without oxygen.
2. Temperature--Usually 450<sup>0</sup> to 800<sup>0</sup>C depending on the metal or alloy.
3. Form--Localized or general pitting and/or general overall surface wastage; sub-surface usually only partially carburized.
4. Product--Dust or powder composed of graphite mixed with metal, metal carbides and metal oxides.

This type of attack includes a broad range of not only deterioration reactions, but catalytic reactions which may occur under certain conditions. For example, Tropsch and Von Philippovich<sup>(2)</sup> and later Fischer and Bahr<sup>(3)</sup> reported the active catalytic behavior of certain metals to the reaction of carbon monoxide, carbon dioxide plus graphite. The work of Bauklow<sup>(4,5,6)</sup> and his associates since then have added much to the information available on this behavior. In 1945, Camp, Phillips and Gross<sup>(7)</sup> of the Humble Oil Company presented the first thorough evaluation of metal wastage in hydro-carbon-carbon monoxide atmospheres. Stainless steel furnace tubes in a super heater for reforming of naphtha in the production of butadiene, operating at approximately 1300<sup>0</sup>F, were the subject of severe metal wastage, both by uniform thinning of the pipe cross-section and by pitting. About the same time Dr. Prange<sup>(8)</sup> at Phillips

Petroleum Company initiated a study of similar phenomena. In 1959, the National Association of Corrosion Engineers devoted an entire session to the metal dusting reaction. This was the first comprehensive attempt to evaluate this unusual form of metal wastage. Papers by Prange<sup>(9)</sup>, Eberle and Wylie<sup>(10)</sup> and Hoyt and Caughey<sup>(11)</sup>, discussed a number of severe corrosion experiences in the 300 and 400 series stainless steels subjected to CO and hydro-carbon atmospheres in the temperature range of 800<sup>0</sup> to 1300<sup>0</sup>F.

A wide range of reaction kinetic studies has been performed at Georgia Tech for iron, nickel, cobalt and their alloys in carbon monoxide, methane, mixed atmospheres of carbon monoxide and hydrogen, methane and hydrogen and higher hydrocarbons. In general, the maxima of the CO reactions are at much lower temperatures than the methane attack. The latter is generally confined to higher temperatures more normal to carburization attack. However, studies of pure butane indicate a practically analogous attack to that found for carbon monoxide. The Butane reaction can be considered similar to that of pure carbon monoxide both in temperature range of reactivity and the temperature of maximum reactivity, but butane is generally an order of magnitude higher in its reactivity.

A partial review of these studies is provided in a report prepared by Hochman<sup>(12)</sup> for the National Association of Corrosion Engineers. This review also includes data and information on a range of reactions and a thorough review of the thermodynamics of possible reactions in the various atmospheres. Details of these studies are contained in a series of theses and papers from the metal dusting study group at Georgia Tech.<sup>(13-23)</sup>

Inhibiting effects have been observed in sulfur and ammonia gases and utilized in a number of petrochemical reactions. Alloys which contain one or more of the

principle nitride formers, i.e., chromium, vanadium, molybdenum and aluminum have shown resistance to metal dusting if sufficient ammonia is present to maintain a nitride surface layer. More common is the inhibition by sulfur in the form of sulfur bearing bases, which in a range of compositions are capable of reducing carbon formation and deterioration in many alloys, particularly iron based materials. In addition, water vapor and in some cases small amounts of volatile metals such as B, As, and Sb in the gas stream seem to give some relief from general attack. Water vapor and/or small amounts of oxygen basically assist in preventing attack on materials with passive qualities by forming stable oxide films.

The effect of pressure has only been examined in a cursory fashion to date. The experiments were mostly at reduced pressure, and little or no effect has been shown on the maximum deterioration temperature unless a partial pressure change of the gases involved results in a change of the thermodynamic stability. Work by Hass et al.<sup>(24)</sup> at atmospheric and slightly elevated pressures has shown that increasing pressure does indicate a change in activation energy and a change in the amount of carbon deposition. Work here at Georgia Tech also has shown increased activation energy but heavy carbon deposition on iron base materials in carbon monoxide in the same temperature range. Both works have shown a general pressure dependence on the initial rate deposition similar to the Hinshelwood-Langmuir type of empirical rate equation where the rate of reaction is:

$$R = \frac{K_1(P_{CO})^2}{k + K_2(P_{CO})^2}$$

where  $K_1$  and  $K_2$  are combined reaction rate constants and the chemical absorption equilibrium constant. Although some preliminary deductions can be made from

pressure studies to date, a marked lack of data and information is noted on the metal dusting reaction as a function of increasing pressures, particularly in the 20 to 100 atmosphere region important to coal gasification processes.

During the past ten years great emphasis has been placed on the development of new or improved processes for the gasification of coal.<sup>(25,26)</sup> These processes have not been adequately tested in respect to structural materials, and little or no data exists concerning the metal dusting of steels and other materials at the high pressures used in the various coal gasification processes. It is imperative that such data be obtained for proper selection of structural materials and prevention of catastrophic failures. The types and quantities of impurities in the gases as well as inhibitors for deterring the reaction under process conditions must also be evaluated for optimum operational conditions and best performance.

#### EXPERIMENTAL WORK

A high-pressure high-temperature reactor was developed in cooperation with the Parr Instrument Company. It is anticipated that with this reactor we will be able to carry out the gas-metal reactions over the entire pressure range and entire temperature range proposed (pressures up to 100 atmospheres and temperatures to 1500°F). The reactor has also been designed to avoid catastrophic corrosive attack on the pressure system. Therefore, it should speed up the investigations, since it has made unnecessary the design and construction of a preliminary non-corrosion-resistant high pressure reactor. It was originally thought that such a step-wise approach would be necessary.

This developed high-temperature, high-pressure reactor was custom built by the Parr Instrument Company and delivered to us in July. The reactor consists of a 500 ml cylindrical autoclave with a small internal furnace. The head and outer

cylinder of the autoclave is constructed of Monel 400. There is Mullite insulation between the outer walls of the autoclave and the internal furnace to keep temperatures of the outer walls at a minimum. Water cooling of the outside surface of the autoclave can be applied when necessary. The internal furnace has a cylindrical reaction chamber which is 1.250 in. in diameter and 4 in. high. The reaction gas is fed through the head of the autoclave, impinges on the sample in the reaction chamber, and exits at the bottom through a valve. In addition to the gas line, two electrodes for the heating elements of the furnace and two thermocouples are fed through the head of the autoclave. The electrodes have high-temperature lava sealants, stainless steel bodies and a special high nickel alloy electrode core. This alloy is one commonly used for spark plugs. The thermocouples is chromel-alumel, and the thermocouple protective sheaths are made of Hastalloy C. The mounting fittings on top of the autoclave for the thermocouples also have stainless steel bodies. One thermocouple reaches into the reaction chamber, and the second one senses the temperature at the autoclave outer wall. The autoclave is further equipped with a Gage Block Assembly with a pressure gage to measure the internal gas pressure. The inside surfaces of the autoclave outer walls are gold plated for corrosion resistance.

The high-pressure system received from the fabricator was assembled. Also, the test stand was set up in preparation for shakedown runs to be carried out.

In addition, a special corrosion-resistant atmospheric pressure reactor was designed and constructed for evaluating the effect of inhibitors on metal dusting corrosion. This reactor consists basically of a quartz tube with Vycor fittings welded to each end. Pyrex headers are vacuum sealed to these fittings for in- and outlet of the gases. A small diameter quartz thermocouple sheath welded to one of

these headers extends to the center of the reaction tube, so that a thermocouple placed in the sheath can sense the temperature of the sample.

Shakedown runs of the atmospheric reactor were conducted, followed by the beginning of the pure metal-gas reaction studies. In the area of inhibitors, work was also performed to improve the methods of approach for this portion of the research.

The shakedown runs for the atmospheric reactor were in two separate areas: The first was a study of the reaction of 316 SS with C.P. grade CO (99.3% pure). These tests were conducted at a constant flow rate of approximately 40 cc/min. Despite some inaccuracies in the data, a curve of the expected shape of reactivity versus temperature was obtained. A curve of the results is shown in Figure I.

Following these initial shakedown studies a program to determine the optimum flow rate for the reactor were initiated. The data indicated a straight line dependence of the reaction rate on the flow rate as shown in Figure II. It was found by means of a linear regression that the line was straight and significant at the 99.99 percentile level. The solid line shown in the figure and representing the dependence of reactivity on flow rate fits the equation:

$$\gamma_i = - 1.091 \times 10^{-4} + 2.424 \times 10^{-5} x_i$$

where  $\gamma_i$  is the weight gain in grams per square centimeter and  $x_i$  is the flow rate in cubic centimeter per minute.

This finding that the reactivity is linearly dependent on the flow rate (up to 75 cc/min. or more) is significant and must be taken into consideration when evaluating metal dusting in coal gasification systems. For our future runs, a flow rate must be arbitrarily chosen on the basis that it will give sufficient reaction and use the least gas.

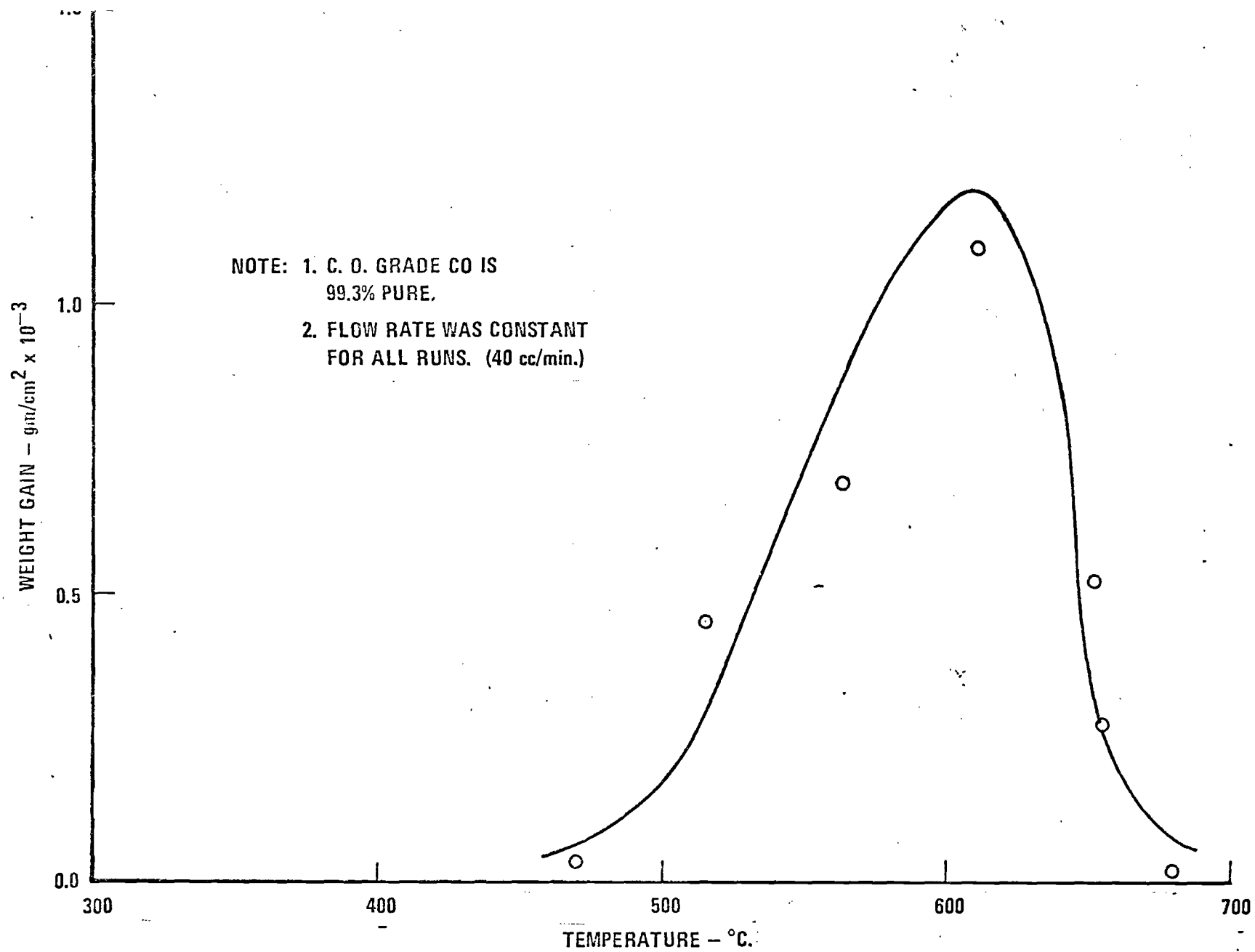


FIGURE I. 316 SS REACTED WITH C. P. GRADE CO.



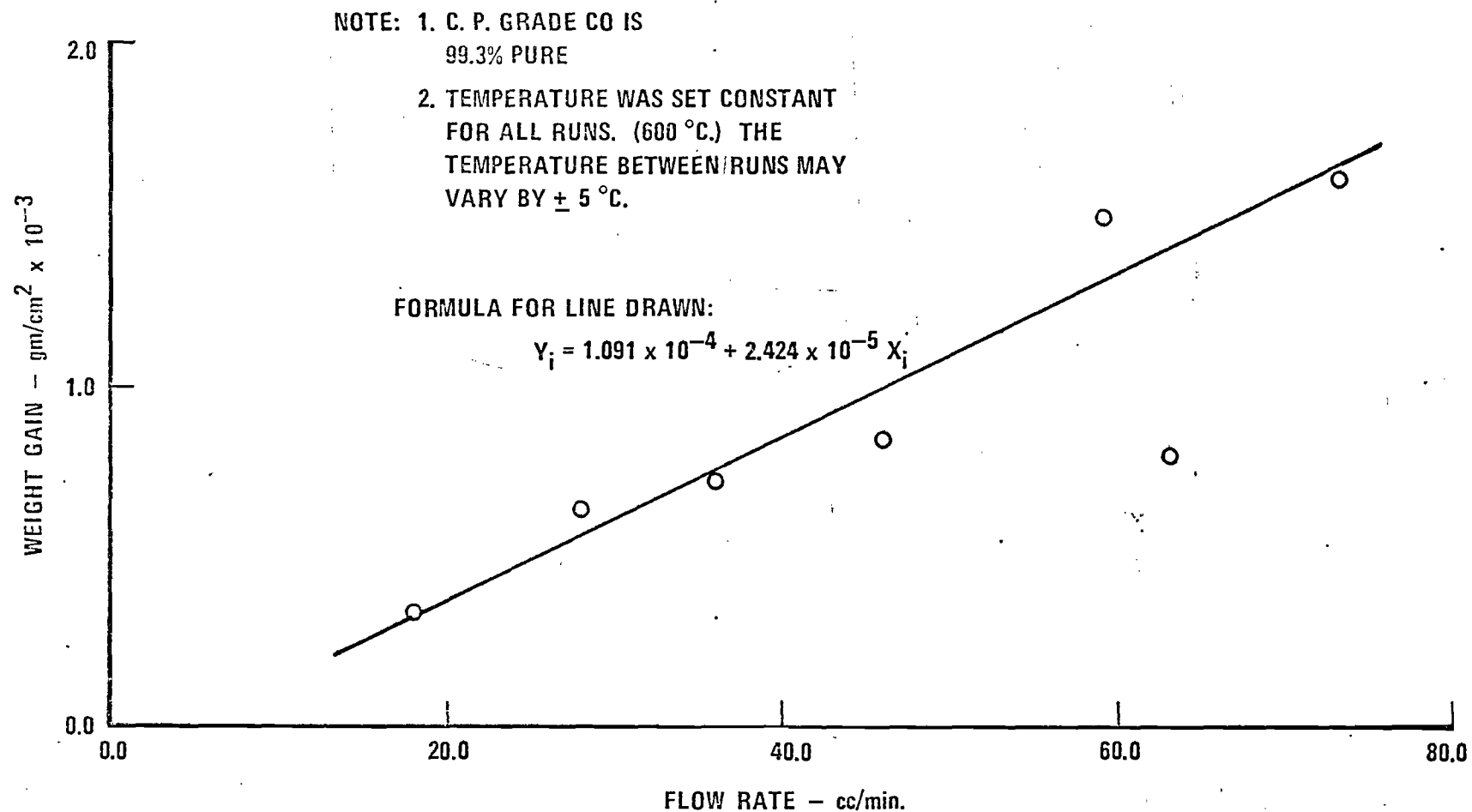


FIGURE II: 316 SS REACTED WITH C. P. GRADE CO.

In the first of the pure metal-gas reaction studies, pure iron was reacted with Ultra High Purity CO (99.98% pure). The results of this series of the run were much more reproducible than those of previous tests. As shown in Figure III, the data fit a smooth curve, despite what is felt as a lack of an efficient cleaning procedure as yet. The data is shifted very slightly to lower temperatures and appears to indicate a higher reactivity than that reported by Westerman<sup>(15)</sup>, although still in good experimental agreement. The greater reactivity can be explained by the method of sample exposure. Westerman used a sample boat which could lead to a shielding of a portion of the sample from the reacting gas. In this apparatus the sample is suspended directly in the reacting gas stream.

#### FUTURE WORK

The project was funded for one year rather than two years, as originally requested. This, of course, has necessitated some revisions and curtailments in the experimental work. Personnel shortages in the beginning and some unexpected legal problems have also had an adverse effect on the project.

However, to offset this, the design construction and shakedown of the planned simplified high-pressure reactor could be bypassed. We were able to immediately design and construct the final high-pressure corrosion resistant reactor. This change in plans should result in significant savings of time and effort.

The immediate objectives of the experimental work for the next quarter will be to (1) expand the pure iron-carbon monoxide curve at atmospheric pressure. (2) Start work in the high-pressure region of the pure iron-carbon monoxide reaction and (3) overcome the problems in the inhibitor phase of the project.

In reference to the high-pressure experiments, shakedown runs with the high-pressure high-temperature reactor will be carried out as a next step to study the

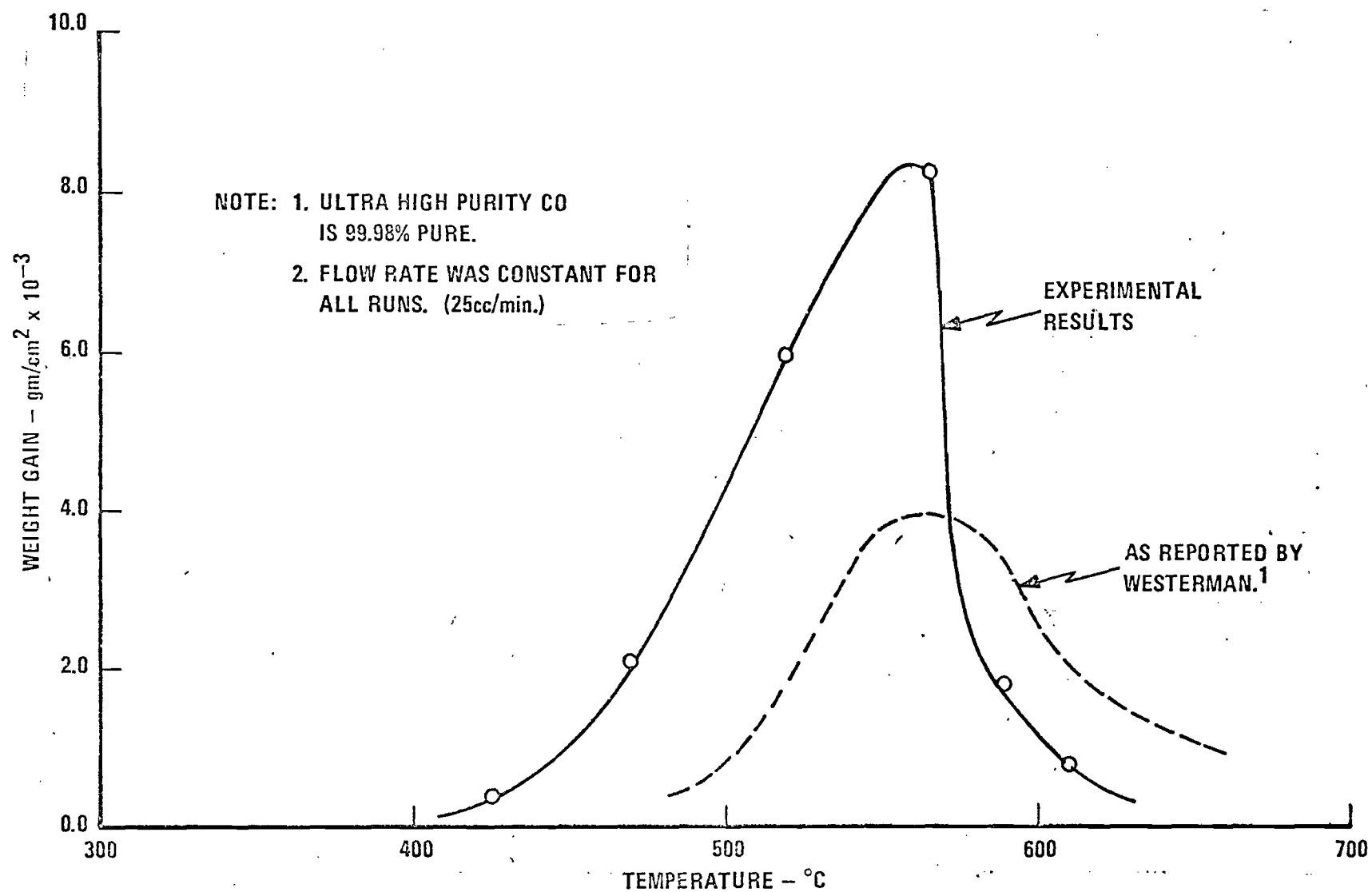


FIGURE III: PURE IRON REACTED WITH  
ULTRA HIGH PURITY CO.

effects of pressure on metal dusting. The initial runs will be made at 150 psig to determine the soundness of the test system and test procedures.

The planned inhibitor studies have been slowed by the problem that the gas mixtures that are of initial interest cannot be legally mixed in conventional containers. Therefore, alternate forms of containers for the reacting gases and inhibitors are being considered and will be tested.

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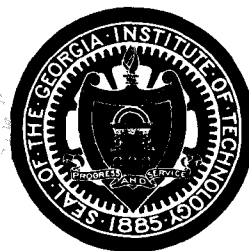
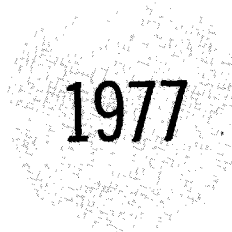
**EFFECTS OF HIGH PRESSURE AND INHIBITORS ON METAL DUSTING  
CORROSION PERTINENT TO COAL GASIFICATION SYSTEMS**

**BY**

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Atlanta, Georgia**

**FINAL RESEARCH REPORT  
GRANT NO. G0155088  
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**Prepared for**

**BUREAU OF MINES  
WASHINGTON, D.C.**

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## PREFACE

This report represents studies initiated on the Bureau of Mines' Grant No. G0155088. The original program was planned for two years, however, funding was not available for the second year due to reorganization of the Bureau of Mines' program in Materials Research for Coal Gasification Systems. The first year consisted primarily of equipment construction and initial test runs, however, with a number of outside fellowships it was possible to continue further indepth research. This report represents the results of not only the first year of Bureau of Mines' research, but approximately 1½ years follow-on of graduate research under the author's direction. Although delayed, this report represents a much more significant package of research than the one year program encompassed by the Bureau of Mines Grant.

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Georgia Institute of Technology  
School of Chemical Engineering, Metallurgy Program  
Grant No. G0155088  
For Bureau of Mines, U.S. Department of the Interior

EFFECTS OF HIGH PRESSURE AND INHIBITORS ON  
METAL DUSTING CORROSION PERTINENT TO  
COAL GASIFICATION SYSTEMS

INTRODUCTION

The conditions of environment, material and temperature in many portions of coal gasification systems portend possible catastrophic deterioration of the metal or alloy by "metal dusting." Studies of this type of deterioration have been carried out over the past seventeen years. However, two areas which are of considerable importance for materials in coal gasification systems have received only limited study. Therefore, a two-phase systematic research program was initiated on March 1, 1975, addressed to these two areas: (1) the effects of pressure on metal dusting and (2) the evaluation of inhibitors added to the gas in deterring the reaction.

The work reported herein covers the first year of this program and an additional extension for student support only. The program was sponsored by the Division of Metallurgy of the Bureau of Mines, U.S. Department of the Interior under Research Grant No. G0155088. Additional research support by institutional fellowships is also included.

BACKGROUND

The deterioration of metals in gases containing carbon at elevated temperatures below normal carburizing temperatures has been termed "metal dusting." The resultant powder-like corrosion product, consisting of carbon

(graphite) and metal, is the basis for the term "metal dusting." The gaseous phases are carburizing and can contain carbon monoxide, carbon dioxide, hydrocarbons, and often water and hydrogen. Iron, nickel, cobalt and most of their alloys are subject to this attack. The form that this attack takes includes localized or general pitting and/or general overall surface wastage. The temperature range for attack is usually from 450°C to around 900°C. Failures have occurred in the petroleum and petrochemical industries, the steel industry, in internal combustion engines, in waste heat boilers, and in certain nuclear reactors. An example of this attack is shown in Figure 1, the deterioration of an iron coil in a hydrocarbon atmosphere.

Crude petroleum processing equipment has often been severely attacked. Sulfur content of the crude has been recognized as the major factor in controlling catastrophic corrosion; but as early as 1937, it was realized that sulfur content was not a direct measure of corrosion tendencies.

Camp, Phillips and Gross<sup>1</sup> reported one of the early cases of catastrophic metal dusting corrosion. Their investigation was concerned with the failure of 304 stainless steel cracking tubes in a butadiene plant, contrasted to a similar plant where corresponding pipes had an excellent record of corrosion resistance. Inspection of the tubes showed they were carburized, but the major deterioration was due to heavy pitting and uniform attack. Their studies indicated that in the plant where the 304 stainless was not attacked, a small amount of sulfur acted as an inhibitor to deterioration.

An earlier well documented report by Burns<sup>2</sup> appeared in 1950 and related heavy corrosion to low sulfur in the crude charges. One curious aspect is that the case presented occurred in new equipment, while an exact duplicate of

the process had performed acceptably for several years. The carbon steel equipment operated for less than a year with several major shutdowns. Many replacements were required due to severe pitting. Burns determined that temperature was the most significant variable. Although the operating temperature was only 300°C, hot spots of 750°C were indicated. Major blame is placed on the iron sulfide found, but mention is made of sooty carbon deposits in and around the corroded area and it is believed that this is a case of "metal dusting."

In 1946 Hubbell<sup>3</sup> noted a problem of aircraft exhaust manifolds subject to carbon and carbon monoxide attack at high temperatures.

In 1959 Hoyt and Caughey<sup>4</sup> cited a case of metal dusting corrosion which was the first in a series of articles on the subject appearing during the next four years. The deterioration of 310 stainless steel in a process producing gasoline from coal was reported. The attack was first observed after 125 days at temperatures of 650° to 700°C, but various types of corrosion were noticed at different times and in various places. Intergranular attack, as well as severe pitting and general metal loss were found. Attack was inconsistent in the same tube. He concluded that optimum conditions vary from gas to gas and theorized that the metal is corroded away by threads of carbon which are attached to metal particles and are easily lifted from the surface and carried away.

Prange<sup>5</sup> investigated stainless steels in corroding gas atmospheres and commented on the complex nature of the problem. He concluded that oxidation was not the significant cause, since copper, which possesses poor oxidation resistance, is not attacked. Corrosion was found to be localized; small

changes in composition resulted in large differences in resistance of an alloy. Prange postulated an unstable vapor phase as the intermediate in the deterioration.

Eberle and Wylie<sup>6</sup> exposed AISI Types 310 and 347 stainless steel to the combustion products of methane at various temperatures. At 900° to 1000°C, intergranular oxidation was blamed for the corrosion. With decreasing temperature, heavy carburization was accompanied by occasional oxide formation. The severest attack was at approximately 600°C. Cyclic carburization, oxidation and reduction were deemed the probable cause of the wastage. Since materials most resistant to carburizing displayed the best performances, carburization was considered a major factor.

A case of heavy pitting in chromium-nickel alloy steel is mentioned by Merrick<sup>7</sup> in 1960. The reddish brown pits were formed in a temperature range of 750° to 1100°C. In contrast with the experience of Burns<sup>2</sup> work with carbon steel, the presence of sulfur did not seem to affect the corrosion rate. The  $\text{CO}_2/\text{CO}$  ratio is concluded to be a determining factor; any value above two was stated as safe, but variances were noted. Experience in their pilot plant showed that a ratio of 0.2 was highly corrosive.

Hopkinson and Copson<sup>8</sup> reacted iron-nickel-chromium alloys in simulated industrial atmospheres consisted of varying amounts of  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{H}_2$  and  $\text{H}_2\text{O}$ . Three different types of attack were observed; (1) pitting under carbon deposits, (2) internal oxidation without free carbon, and (3) heavy carbon deposits with exfoliation-characteristic of metal dusting. Although some conclusions are presented, the part played by carbon and carburization in the mechanism of attack could not be clearly defined.

Lefrancois and Hoyt<sup>9</sup> presented an article on the subject of metal dusting with a thermodynamic analysis. Three distinct cases of metal dusting in stainless steels were examined to determine the compounds comprising the corrosion deposits and to deduce their morphology. In two of the cases,  $M_{23}C_6$  and/or  $M_7C_3$  were discovered; carbon soot and metal oxides were found in the pits of the third sample and a protective silicon oxide was found on the unblemished surface. All three cases exhibited severe pitting. From the results only a negative analysis was possible; iron and its oxides were deemed not principals, cementite, nickel carbide and the carbonyls were eliminated on the grounds of thermodynamic instability and the carbides,  $M_{23}C_6$  and  $M_7C_3$  by their presence, were associated with the mechanism of metal disintegration.

Hochman and Burson<sup>10</sup> published work in which the major forms of the attack are discussed. The reactivities of iron, nickel, cobalt and their alloys are also presented for a wide range of temperatures.

The basic mechanism of the graphitization by CO and the  $2CO \rightarrow CO_2$  (Boudouard) reaction has received much more attention than the metal dusting reaction. It is important to note that this type of attack includes a broad range of not only deterioration reactions, but catalytic reactions which may occur under certain conditions. For example, Tropsch and Von Phillippovich<sup>11</sup> and later Fischer and Bahr<sup>12</sup> reported the active catalytic behavior of certain metals to the reaction of carbon monoxide, carbon dioxide plus graphite. The work of Bauklow<sup>13,14,15</sup> and his associates since then have added much to the information available on this behavior. Other prominent studies of catalytic effects on this reaction were published by Juliar, Rayet and Lude,<sup>16</sup> Davis, Slawson and Rigby,<sup>17</sup> Kagan, Bashkirov, Kamzolkina and Rozovsky,<sup>18</sup> Das and Chattergee,<sup>19</sup> and Walker, Rakszawski and Imperial.<sup>20</sup>

The effects of small additions of  $H_2O$ ,  $H_2$  and  $O_2$  have also been examined. In the work of Walker, Rakaszewski and Imperial<sup>20</sup>, a comprehensive study of the reaction of  $CO-H_2$  mixtures over an iron catalysis was made. From  $470^\circ$  to  $570^\circ C$ , the  $H$  concentration effect is small, but from  $570^\circ$  to  $639^\circ C$ , it is more pronounced. In an isolated case, pure  $CO$  was reacted and found to be substantially less reactive than the mixture. Baukloh and Henke<sup>21</sup> stated that water retarded the decomposition of  $CO$  over iron. Akamatsu and Sato<sup>22</sup> noted that traces of  $O_2$  and  $CO$  at  $500^\circ C$  retarded the reaction on iron plate but not with iron powder.

A more complete compilation of literature is available in a bibliography Hochman, Ratliff and Westerman<sup>23</sup> published by NACE and a more thorough review in monograph form is now in preparation by the author.

Research in the area of metal dusting generally has been aimed at defining the products formed, the reactivity, and the reaction kinetics for systems consisting of the common engineering alloys and the simpler metal dusting environments (gas phases of carbon monoxide, methane, and their mixtures with hydrogen). The reaction of carbon monoxide on iron under controlled conditions has been the most studied of the metal dusting forms of attack. Because of this, the kinetics and some mechanistics of carbon monoxide metal dusting has been determined.

A second form of metal dusting, hydrocarbon attack, has also been studied mostly using methane as an environment. And more recently butane. Although the hydrocarbon methane has been considered as contributing to the reaction, this pure hydrocarbon gas had been shown experimentally to have only minimal reactivity at metal dusting temperatures.



At each temperature the deterioration of the loss of weight of the metal surface is proportional to the weight of carbon formation. The carbon formed consists of: (1) filamentary growth, and (2) flake or bulk deposits. The length and diameter of the filaments increase with increasing temperature. Above the eutectoid temperature surface deterioration stops and only a small amount of carbon is deposited.

In general the sequence in metal dusting of iron in CO has been experimentally determined, however, many factors are still not understood and the many reasons why still remain to be determined before detailed metallurgical developments can be brought to bear. To best review the reaction a summary of the CO attack on iron proceeds by the following steps:

- A. Absorption of carbon monoxide.
- B. Breakdown of carbon monoxide, the Boudouard reaction ( $2\text{CO} \rightarrow \text{CO}_2 + \text{Carbon}$ ). This is probably rate controlling in the initial stages of the reaction.
- C. Absorption of carbon into the surface by diffusion. This is rate controlling in the latter stages of the reaction.
- D. Buildup of carbon in the solid solution and decoration of dislocations and subgrain boundaries with carbon.
- E. Precipitation of cementite at areas of higher carbon concentration.
- F. Growth of cementite without other forms of carbide formation.
- G. Having reached the critical concentration of cementite in the ferrite matrix, the cementite decomposes, regenerating carbon and iron plus the precipitation of subcarbides.

H. The deterioration of the base metal occurs by the continued precipitation of graphite with the growth of the decomposition products.

Reactions on iron base alloys and on nickel and cobalt, with some slight changes probably have a similar mechanism. Therefore the following portion of this paper is devoted to an examination of this sequence of reaction steps, how they occur and possible deterrents.

The effect of pressure has only been examined in a cursory fashion to date. The experiments were mostly at reduced pressure, and little or no effect has been shown on the maximum deterioration temperature unless a partial pressure change of the gases involved results in a change of the thermodynamic stability. Work by Hass et al.<sup>24</sup> at atmospheric and slightly elevated pressures has shown that increasing pressure does indicate a change in activation energy and a change in the amount of carbon deposition. Work here at Georgia Tech also has shown increased activation energy but heavy carbon deposition on iron base materials in carbon monoxide in the same temperature range. Both works have shown a general pressure dependence on the initial rate deposition similar to the Hirnshelwood-Langmuir type of empirical rate equation where the rate of reaction is:

$$R = \frac{K_1 (P_{CO})^2}{k + K_2 (P_{CO})^2}$$

where  $K_1$  and  $K_2$  are combined reaction rate constants and the chemical absorption equilibrium constant. Although some preliminary deductions can be made from pressure studies to date, a marked lack of data and information is noted on the metal dusting reaction as a function of increasing pressures, particularly in the 20 to 100 atmosphere region important to coal gasification processes.

During the past ten years great emphasis has been placed on the development of new or improved processes for the gasification of coal. These processes have not been adequately tested in respect to structural materials, and little or no data exists concerning the metal dusting of steels and other materials at the high pressures used in the various coal gasification processes. It is imperative that such data be obtained for proper selection of structural materials and prevention of catastrophic failures. The types of quantities of impurities in the gases as well as inhibitors for deterring the reaction under process conditions must also be evaluated for optimum operational conditions and best performance.

EXPERIMENTAL EQUIPMENT AND PROCEDURES

## A. High Pressure Research

## 1. Materials

To date all high pressure tests have been run with pure iron wire and pure carbon monoxide. For a detailed listing of the purities and physical characteristics of the iron wire, carbon monoxide and argon purging gas, see Appendix I.

## 2. Equipment

The major item in the high pressure metal dusting system is the monel bomb. See Figure 1 for a schematic diagram of the unit. Though originally designed for use as a batch type reactor, the bomb was modified by the manufacturer to allow the continuous gas flow needed for these studies. The modification was accomplished by drilling an exit port in the bottom of the unit to compliment the gas inlet port already in the head of the unit. An additional modification was made, the inside of the bomb was gold plated to protect the metal walls from the corrosive environment produced as a part of these tests. The head of the unit is sealed to the body by means of a diamond cross section ring that is firmly pressed into grooves in the head and body by pressure bolts that mount in two semi-circular carbon steel sealing collars.

In addition to the gas inlet port, the head of the unit provides an entrance point for two thermocouples and power leads for the heating unit. One of the thermocouples is used to monitor the sample

## Legend for Figure 1

Figure 1:



### Equipment

1. Shut-off control valves.
2. Precision rotameter.
3. Precision, double pattern fine metering valve. Used to control the exit flow rate.
4. Precision fine metering valve used to control the gas flow into the unit during start-up.
5. Quick couple.
6. Stand pipe weir.
7. Cooling tank floor.
8. Block valve.
9. Pressure gauge
10. High pressure unit.
11. Water level.
12. High pressure unit support.



### Ports

1. Exhaust header.
2. Sample port.
3. Vacuum header.
4. Reacting gas input.
5. Inert gas input.

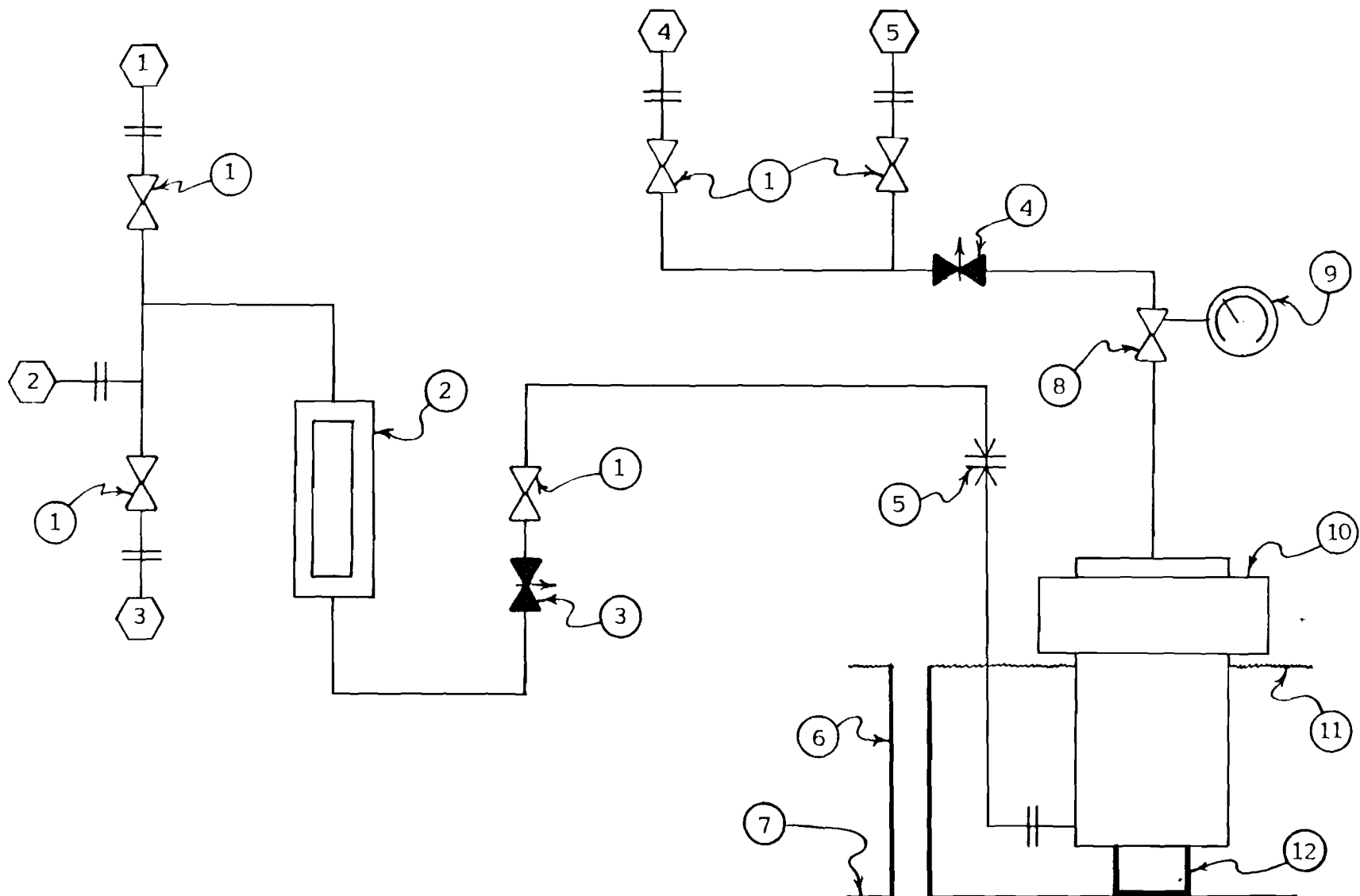


Figure 1. Schematic flow sheet of the High Pressure Unit. See next page for notes and comments.

temperature and as a control signal for the heating coils. The other thermocouple is placed next to the wall of the unit as a safety feature to prevent overheating of the metallic walls of the bomb. The power leads for the heating coils provide an air tight, electrically insulated path for the introduction of the electric current needed to power the heating coils.

Heat is provided by a set of semi-circular, resistance heating units that are connected in series and supplied with a pulsed AC voltage source. The supply voltage can be changed as the power requirement varies.

Ancillary equipment needed to perform the experiment include a custom designed and constructed power controller for maintenance of reaction zone temperature, a precision four inch pressure gauge for monitoring the reaction pressure, high pressure regulators for the control of reaction pressure, a precision flow meter to monitor the gas flow rate thru the reaction zone, a mechanical vacuum pump for removing all air from the unit prior to the start of the reaction, and assorted fine metering and shut-off valves to control the gas flow in the reactor during the run. See Figure 2 for a detailed schematic diagram of the bomb and the flow path through the unit. A photograph of the unit is shown in Figure 3.

### 3. Experimental Procedure

A sample of the wire to be studied was cut to a given length to provide the desired surface area and then coiled around a mandrel.

## Legend for Figure 2

Figure 2:



### Equipment

1. Sealing collars.
2. Wall insulator.
3. Diamond cross section sealing ring.
4. Heating coils.
5. Thermocouple thruputs.
6. Power thruputs.
7. Head of High Pressure Unit.
8. Power lead to heating unit.
9. Sample thermocouple.
10. Wall thermocouple.
11. Reaction zone insulator.
12. Sample hanger.
13. Sample Wire.
14. Clamping bolts.
15. Bolt striker plate.
16. Collar retaining ring.
17. High pressure reactor body.



### Ports

1. Gas exit port.
2. Gas inlet port.



### Electrical connections

1. Sample thermocouple hookup.
2. Power hookup.
3. Wall thermocouple hookup.



Figure 2. Schematic diagram of the High Pressure Unit. A full section. See next page for notes and comments

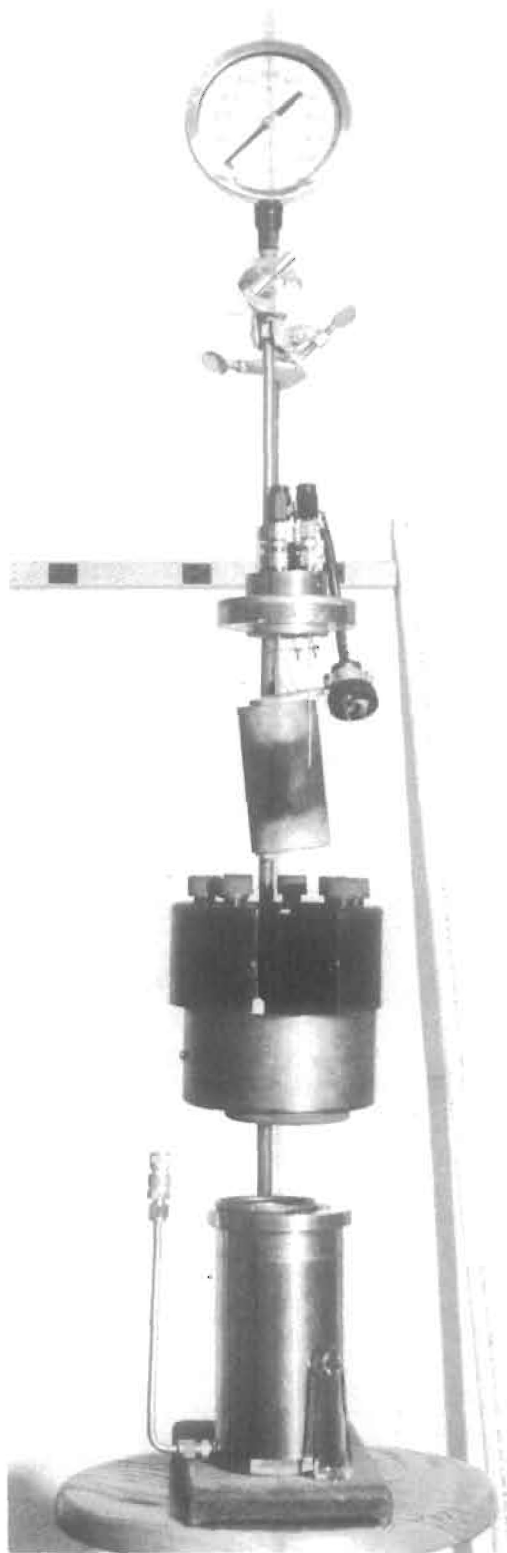


Figure 3. Exploded view of the high temperature reactor.

It is then cleaned in high purity 1, 1, 1 trichloroethane to remove any processing oil that may coat the surface. After cleaning, the sample is weighed, hung in the sample holder, and placed in the unit. The unit is then sealed and placed in the water bath used to prevent overheating of the bomb walls during the run. After all hose, tubing, and power connections have been made, the unit is evacuated by the mechanical vacuum pump for a minimum of eight hours. At this point, the unit is flooded with the desired pressure of ultra-high purity argon. This is done to allow the unit to reach stable reaction conditions before the reacting gas is introduced. The unit is then heated to the desired temperature and allowed to stabilize in pressure, temperature, and flow rate. Once steady state conditions have been reached, the unit is rapidly evacuated of the argon and the reaction gas is introduced into the unit at the desired pressure. During the course of the run all parameters of interest are monitored and recorded.

After the sample has reacted for the desired length of time, the power to the heating coils is cut off and the reacting gas is evacuated from the unit as rapidly as possible without causing damage to the fragile corrosion products found on the surface of the sample. The sample is allowed to come back to ambient temperature while under the vacuum. Once the unit has cooled, it is slowly flooded with air, removed from the cooling bath after all connections are broken, and unsealed with extreme care. Throughout this disassembly operation,

care must be taken to prevent the sample from being shaken, or the corrosion products will flake off and fall into the bottom of the unit. In some instances the sample is in such a fragile condition that it will fall apart if the unit is vibrated. Once the unit has been opened, the sample is removed, weighed, recorded and then placed in a labeled air tight bottle for later reference if desired.

## B. Inhibitor Research

### 1. Materials

The studies conducted have been on pure iron, pure nickel and Inconel 600 wire in mixtures of  $H_2S$  in high purity CO. The materials are more completely defined in Appendix I and in other sections of this chapter.

### 2. Experimental Equipment

The quartz reaction tubes were suspended in a two furnace system. Fundamentally the reactor apparatus is capable of providing a controlled exposure of  $H_2S$ -CO mixtures to both microscopic and macroscopic specimens. The system is designed to operate under steady state gas flow conditions. The wire samples of 5 cm<sup>2</sup> area are wound in circular fashion around a Teflon mandril approx. 6-7 mm diameter. These samples are suspended in chamber in the uniform temperature region of the tubular furnaces. All temperatures are controllable to better than  $\pm 10^\circ$  by using the Leeds and Northrup recorder-controller.

Quartz was chosen for construction material of the reaction zone because it is able to withstand the temperatures involved, and it

does not react with either CO or  $H_2S$ . Strength properties were not a major requisite since the system operates at atmospheric pressure. The conducts providing entrance and exit for the gas flow were fashioned from transparent thick walled high pressure rubber tubing. A schematic diagram of the system is shown in Figure 4 and a photograph of the system in Figure 5.

The device from which the samples were suspended consisted of quartz tubing, max OD, 6 mm, max ID 4mm. and at the end of the tube a hook made of quartz rod. A quartz rod basket was used to suspend two wire samples in each furnace. This facilitated the exposure of 4 samples simultaneously to the same gas mixture at two temperatures, i.e., one Ni sample and one Inconel 600 sample per reactor chamber, hence the more economic use of gas and time. The tubing and basket were constructed to be removable and also to allow samples to be suspended in the region of constant temperature in the furnace. Most of the iron studies were conducted when the system consisted of only one furnace.

### 3. Experimental Procedure

C.P. Grade  $H_2S$  of purity 99.6% and Mathyon Grade CO of 99.99% purity were used for this experimental work. Dry argon was used to purge the system during periods of heating to reaction temperature. All gases were supplied to apparatus from high pressure cylinders. The gas flow rate for all reactions is 22 cc/min measured at ambient conditions of temperature and pressure.

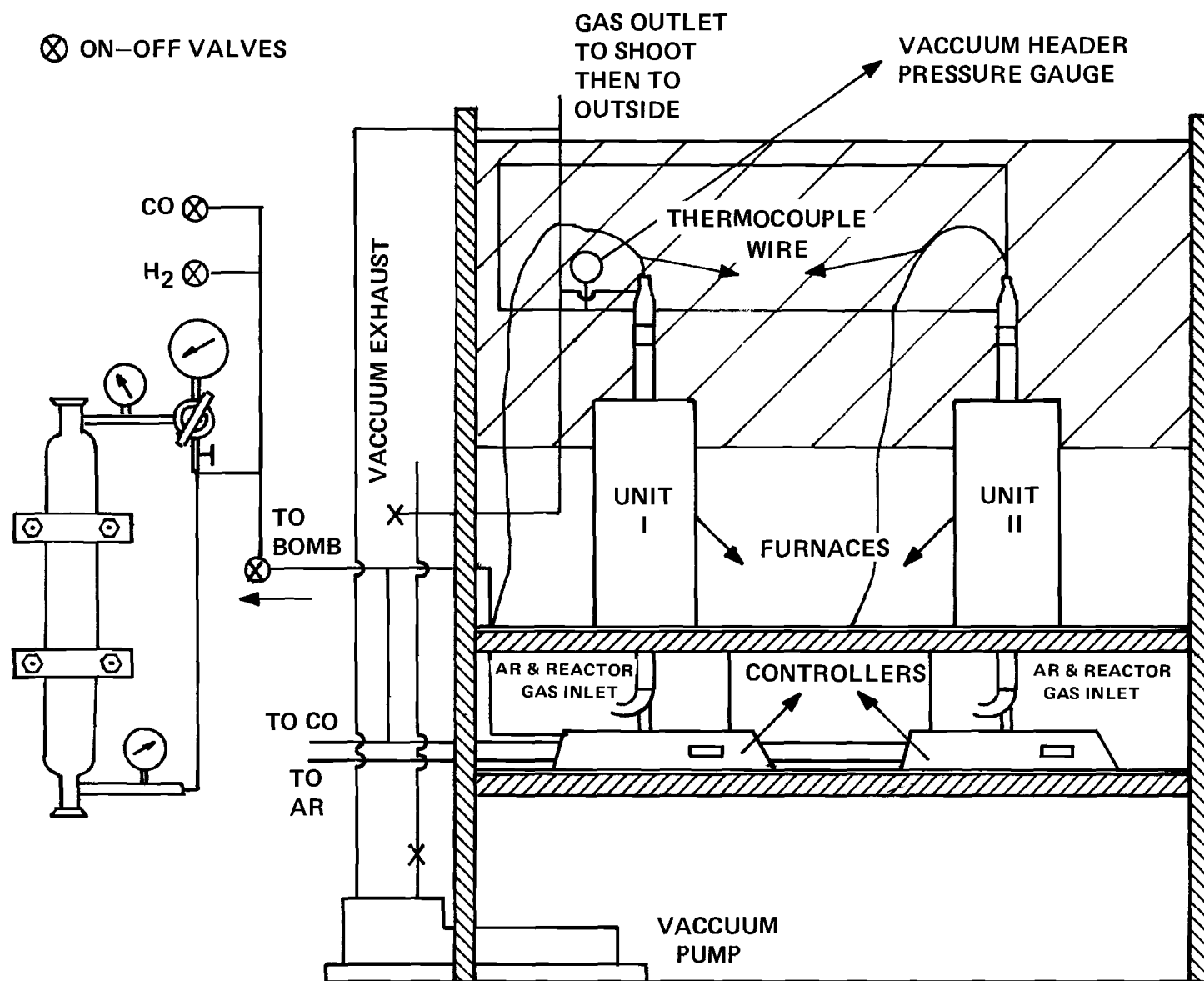


Figure 4. Schematic diagram of the inhibitor gas mixing and reactor system.

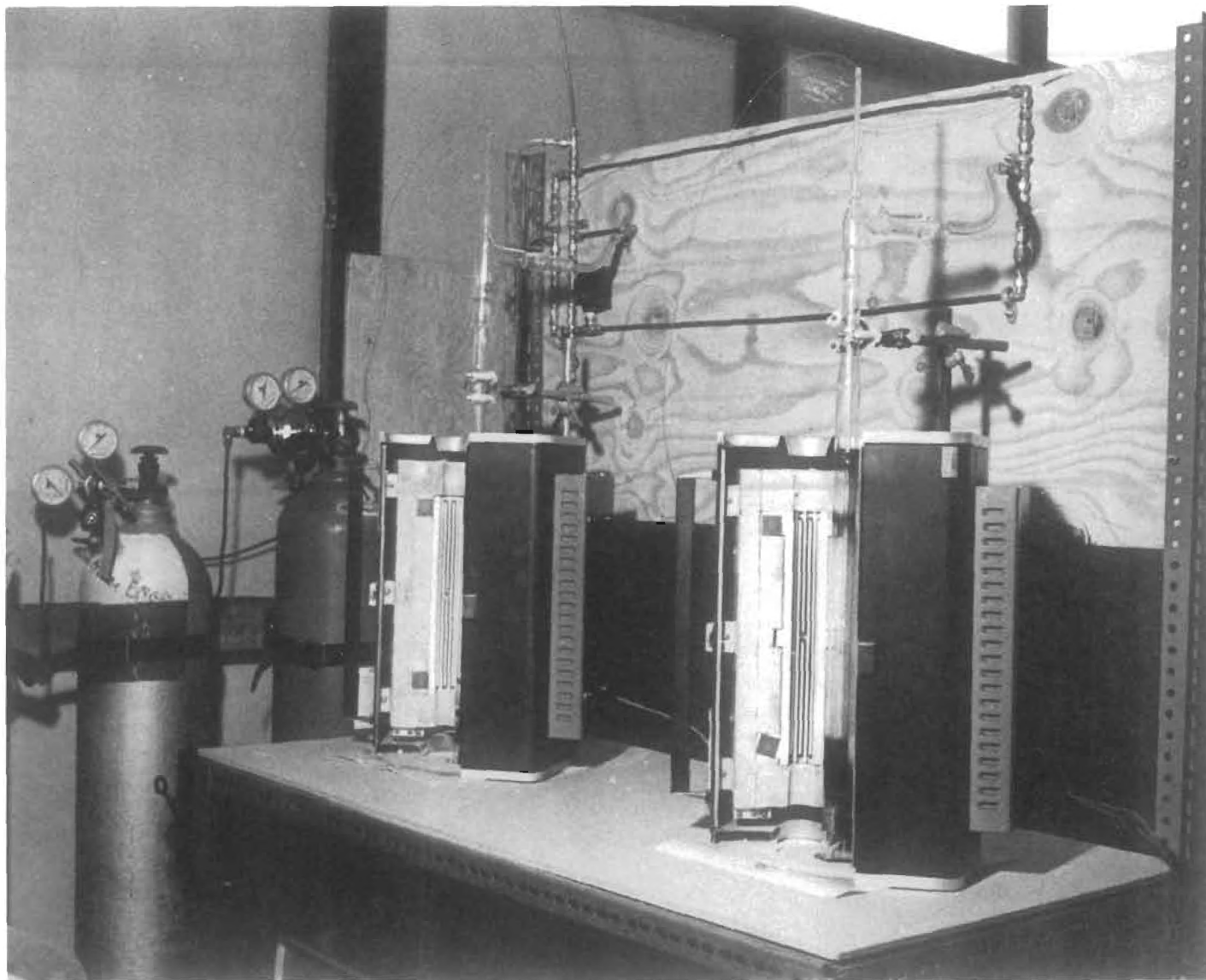


Figure 5. Photograph of the inhibitor reaction system.

## EXPERIMENTAL RESULTS

### A. High Pressure Data

To date the amount of data produced has been limited since a major portion of the first year was spent in equipment construction and shakedown. A large portion of the data reported here has been produced in the last 12 months. The equipment is now functioning exceptionally well and no major problems are being encountered.

The data that has been obtained so far include the following studies. In addition to shakedown and one atmosphere CO standard studies, a curve, made up of eight 20 hour runs, describes the reactivity of pure iron in pure CO at 300 psig as a function of temperature. This data is shown in Figure 6. Second a series of runs at two hour intervals have been made to define the reaction of pure iron with pure CO at 300 psig and 600°C as a function of time. This data is shown in Figure 7. It is expected that these results will help determine the kinetics that are controlling the reaction at these and hopefully other conditions in the high pressure realm. Finally, several runs have been made to determine the effects of pressure increase on the rate of reactivity. Pure iron was reacted with pure CO at 550°C for four hours at pressures of 150, 300, 450, and 600 psig. This study needs to be expanded both as a function of pressure and temperature within the capabilities of the extant equipment. The preliminary results to date are reported in Table I.



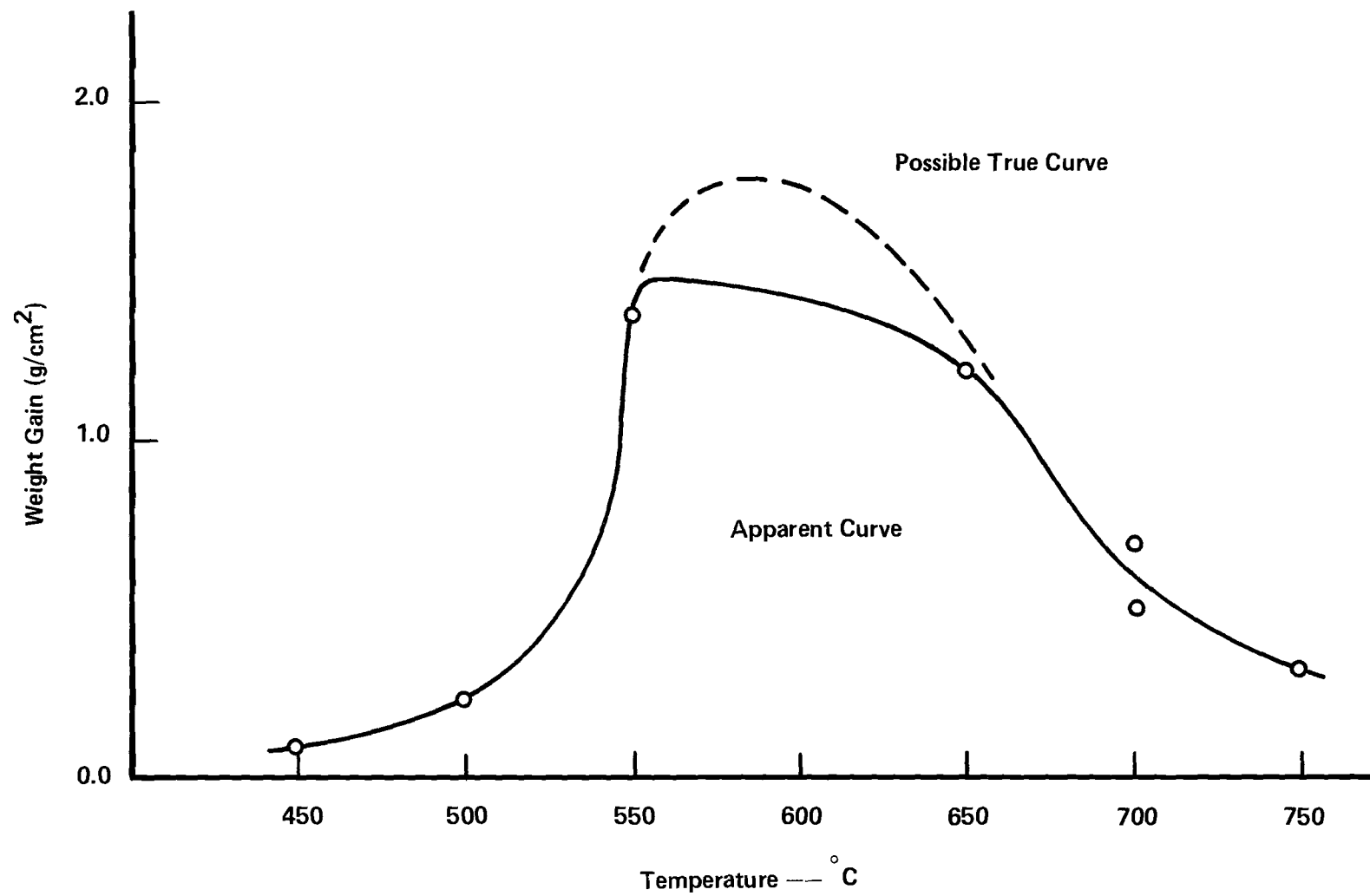


Figure 6. Reaction of Pure Iron with Pure CO at 300 psig. (run time = 20 hours)

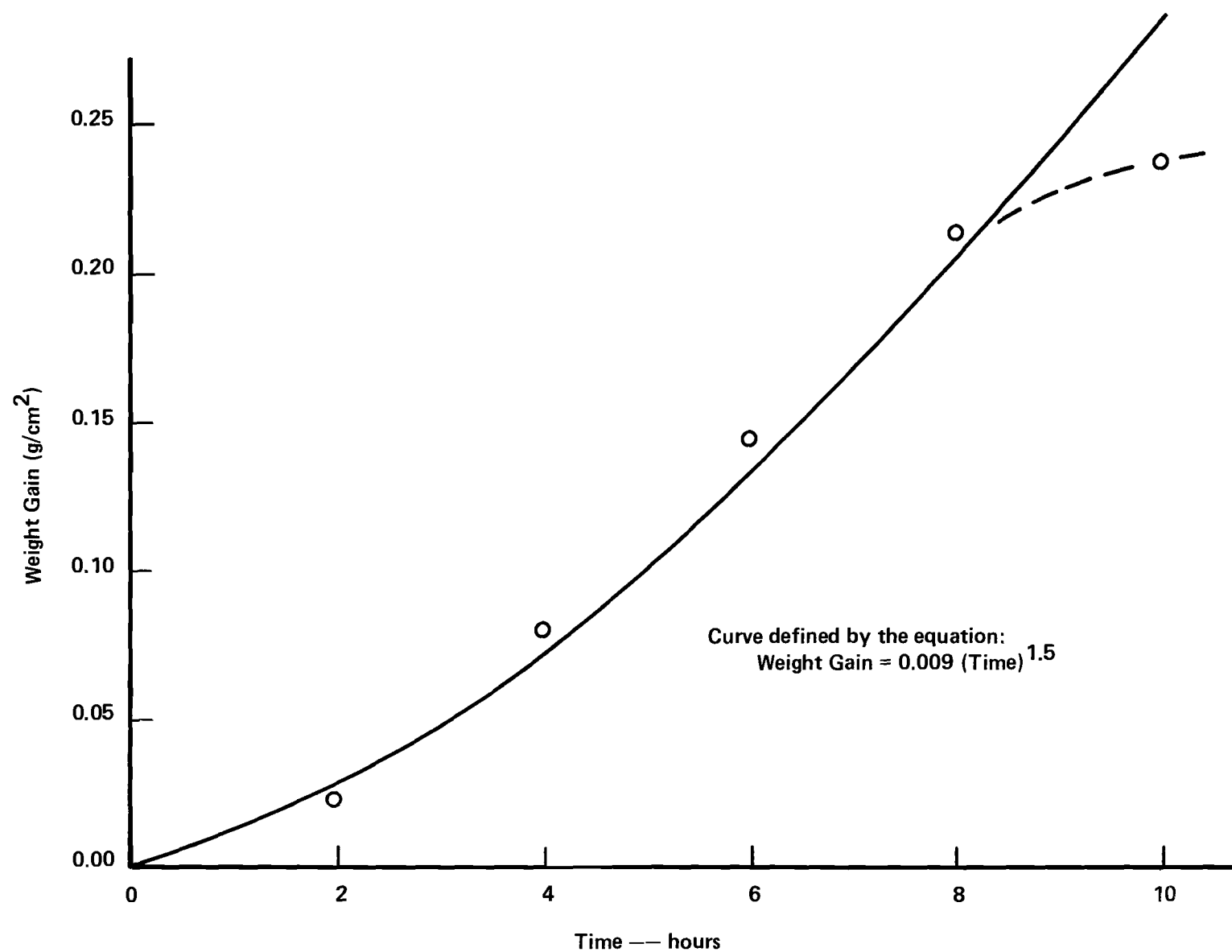


Figure 7. Reaction of Pure Iron with Pure CO at 300 psig and 600°C as a function of time.

TABLE I. REACTION OF PURE IRON WITH PURE CO AT 550°C  
AS A FUNCTION OF PRESSURE. (RUN TIME = 4 HRS.)

Pressure - psig · Weight Gain - g/cm<sup>2</sup>

150	$8.868 \times 10^{-2}$
300	$1.544 \times 10^{-1}$
300	$1.487 \times 10^{-1}$
450	$1.608 \times 10^{-1}$
600	$1.347 \times 10^{-1}$

The experimental procedure deployed in this study is as follows:  
In both cases (all cases) wire samples of the following dimensions are obtained from bulk

Length = 31.33 cm

OD = 0.0503 cm

Surface Area = 5.00 cm<sup>2</sup>

A sample is wound around a cylindrical mandril and a hook is formed at the end. The wire is now coiled in the form of a cylindrical spring. A special distillation apparatus is used to clean samples. After careful mechanical wiping the sample is exposed to 1,1,1-trichlorethane for 20 minutes. Gas mixtures were made in portions of 1000 psi, as that amount of gas was sufficient for generating a complete curve, consisting of 6 to 7 data points. Mixing was done by using a stainless steel cylinder (bomb) with the capacity for 1000 psi of gas mixture. All gas mixture calculations were made assuming the ideal. The pressure of H<sub>2</sub>S calculated corresponding to a specific volume was first expanded into bomb. The bomb was then isolated. All tubing was then evacuated using a vacuum of 10<sup>-3</sup> torr. CO was then forced into bomb to register a pressure of 1000 psi.

The samples were then placed in the reactors and the entire system was evacuated for about 12 hours for every new gas mixture, however, 2 hours was felt satisfactory between data points. Dry argon was then flushed through the system as reactor chambers came to the selected reaction temperatures. Once at experimental temperature, the system was again subjected to a high vacuum for 10

minutes. After which, the reactor gas is allowed to start through the chamber at 200 cc/min. The duration time per reaction is 20 hours. The system is then cooled to room temperature under high vacuum. The wire samples are then removed and their weight gain and/or loss recorded.

## B. Inhibitor Studies

Evaluation of the effect of sulfur as  $H_2S$  in the CO gas stream has been studied as a function of temperature and gas composition for pure iron, pure nickel and Inconel 600. Some additional studies on  $H_2O$  have also been performed but the data is so preliminary that it is not included here. Figure 8 is a set of curves for CO with  $H_2S$  varying from 0 to 100 ppm. Some additional spot checks have been made at high  $H_2S$  compositions but x-ray and electron diffractions verified the onset of heavy sulfidization. This is another corrosion program in itself and hence most of the studies were limited to the work with  $H_2S$  to determine a range where it could be an effective inhibitor to metal dusting corrosion.

The effect of  $H_2S$  on the CO reaction with nickel and Inconel were also evaluated. CO with 2.5 to 1000 ppm of  $H_2S$  were compared to the reactivity of these materials in pure CO. Figures 9 and 10 are curves of the reactivity of these mixtures as a function of temperature.

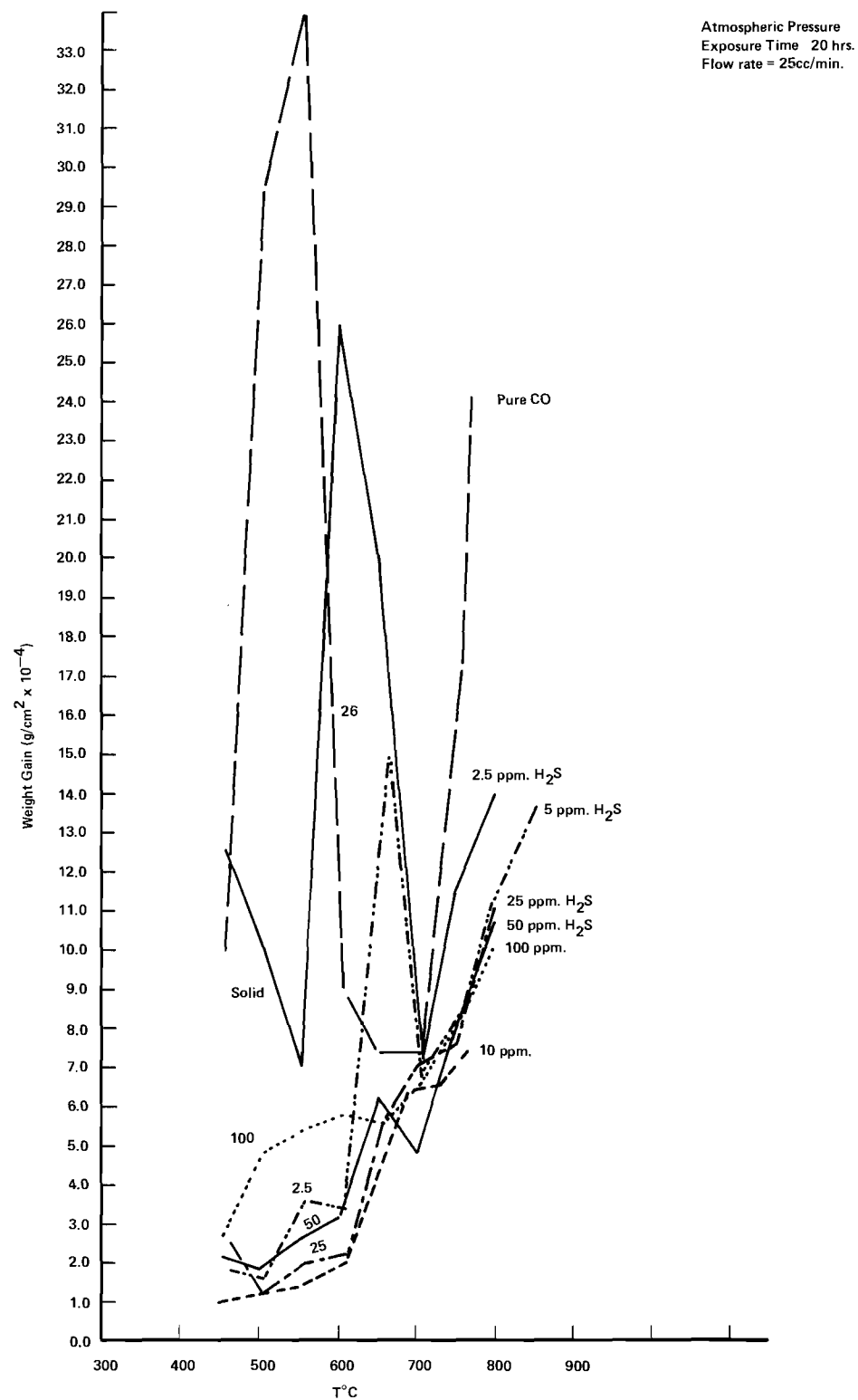


Figure 8. The effect of various concentrations of  $\text{H}_2\text{S}$  on metal dusting reactivity.

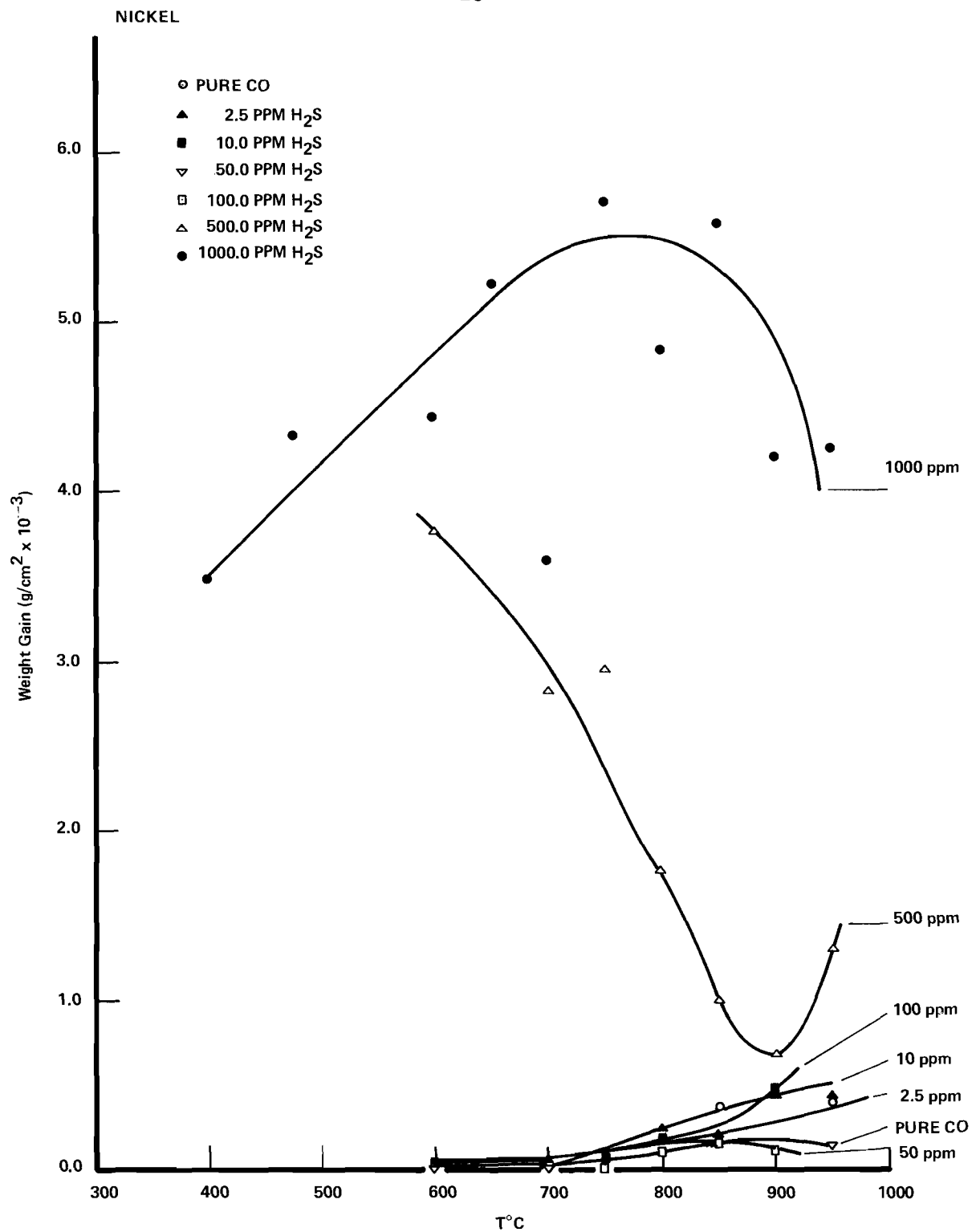


Figure 9. Reaction of nickel in CO and CO-H<sub>2</sub>S mixtures



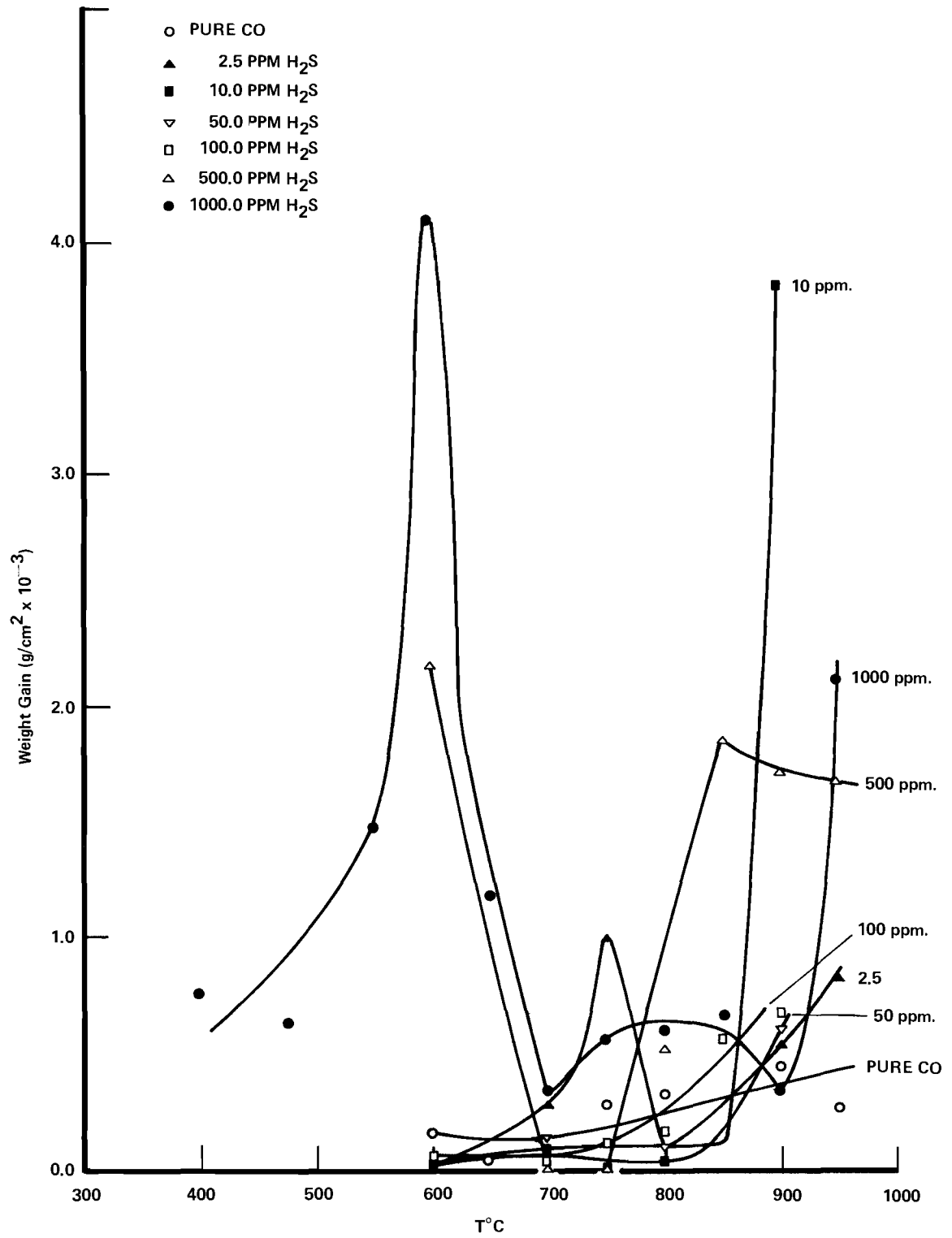


Figure 10. The reactivity of Inconel 600 in CO and CO- $H_2S$  mixtures

## DISCUSSION OF RESULTS

### A. High Pressure Studies

The data obtained for the reaction of pure iron and pure CO at 300 psig as function of temperature at the lower temperatures (500°C or less) and the higher temperatures (700°C or more) are quite accurate; however, the results obtained at the intermediate temperatures are almost certainly too low. In this region of maximum reactivity, the samples were almost completely destroyed. Some actually completely disintegrated and fell into the bottom of the unit at some undeterminable point during the course of the run. The exact magnitude of the corrosion in these regions is not known at this time. These data points do show, however, that the rate of corrosion under these conditions is extremely rapid and catastrophic. For a more accurate determination of the magnitude of the reaction at this pressure, a series of runs of a shorter duration is in order.

An excellent comparison of the difference in reactivities as a function of pressure is shown graphically in Figure 11 and pictorially in Figure 12. The difference in reaction at 1 atmosphere and 300 psig is diamatically illustrated in the choice of representative data depicted in these results.

The study of the kinetics of the reaction of pure iron with pure CO at 300 psig and 600°C has shown an accelerating rate. For the runs of eight hours or less it was determined by an approximate curve fitting procedure that the reaction could be described by an equation of the form  $\text{Weight Grain} = k(T)^\alpha$ , where  $k$  is a constant (approx.  $9.0 \times 10^{-3}$ ),  $T$  is the time in hours, and  $\alpha$  is also a constant (approx. 1.5). For the run at ten hours the rate of

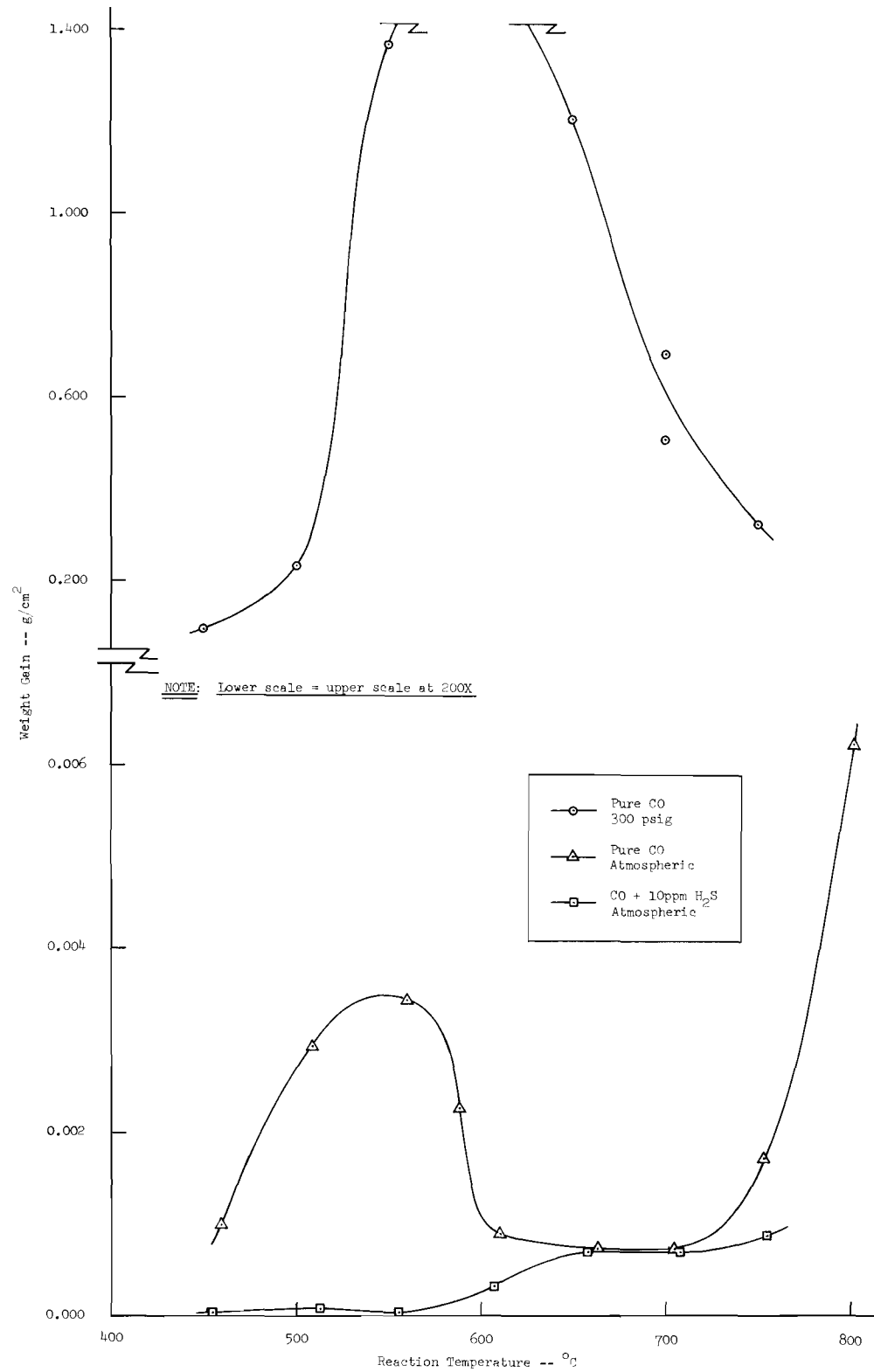


Figure 11. Comparison of metal dusting reactivity of iron in CO at 1 atmosphere and 300 psig as well as in CO with 10 ppm H<sub>2</sub>S at 1 atmosphere.










Pressure	Unreacted Sample	Gas	Reaction Temperature -- °C		
			450	550	750
300 psig (2.0 cm <sup>2</sup> sample)		Pure CO			
Atmospheric (5.0 cm <sup>2</sup> sample)		Pure CO		 1 cm	
		CO + 10ppm H <sub>2</sub> S		NOTE: All sample photos are at the same magnification.	

Figure 12. Pictorial comparison of samples at 1 atmosphere and 300 psig and in CO-10 ppm H<sub>2</sub>S at 1 atmosphere psig at representative temperatures of 450°, 550° and 750°C.

increase in the rate of reaction showed a decrease. Determinations of the nature of the reaction rate for longer duration runs will be difficult, as the sample at ten hours was very heavily reacted. Attempts to make longer runs resulted in the disintegration of the sample.

The results obtained in the kinetics study can be explained by one of two processes. The reaction could be of an autocatalytic nature. This would account for the increasing rate at short times, since the rate of reaction is dependent on the amount of reaction product that is present to help catalyze the reaction. This would also account for the decreasing rate of reaction after eight hours, since a tapering off of the reaction rate will occur as the amount of the pure, unreacted iron is reduced, thereby reducing the amount of material available to act as a reaction site. Another possible mechanism is related to the amount of pure iron surface area exposed to the reaction environment. As the reaction proceeds some of the grains of the sample wire are "floated" out of the body of the wire by the carbon that deposits on the surface and diffuses into the metal. As these grains leave the main bulk of metal, new surface area is created since the entire area of the grain is exposed and new surface area is exposed on the wire itself. The decreasing rate of reaction at times in excess of eight hours could be explained by the limit of available surface area being approached as all of the original wire sample is used up. Which of these mechanisms is in fact the type controlling the reaction rate will have to be determined by a study of the reaction products and the physical condition of the sample as a function of time.

Though the study of the reaction rate as a function of pressure is at present not detailed enough to give an detailed analysis of the function that

describes the reaction, a very significant discovery has been obtained. As the pressure is increased, the rate of reaction also increases, however only a few data points but higher pressure have been obtained but these indicate as further increases in pressure occur, the rate of reaction may decrease. The exact reason for this phenomenon is at present not known since the experimental results are very limited. One possible reason would be a shift in reactive rate maximum and it also appears from the visual examination of the samples studied that the density of the deposited carbon layer increases as the pressure of the reaction is increased. This could build up a barrier to the further deposition of carbon.

## B. Inhibitor Studies

Figure 9 graphically demonstrates the effect of  $H_2S$  as a representative sulfur bearing inhibitor to metal dusting. The 2.5 to 5 ppm  $H_2S$  range reduces the CO reactivity and shifts it to slightly higher temperatures. At 10 ppm, however, a definite inhibition is reached which is essentially good to 50 ppm, then a slow increase in reactivity is again noted. Studies at 100 ppm and above have shown this increase to be the result of the nucleation of sulfide attack. Thus the critical  $H_2S$  for inhibition in this reactor is between 10 and 50 ppm  $H_2S$ . The 10 ppm  $H_2S$  inhibition of the reaction is pictorially and graphically shown in Figures 11 and 12.

It is obvious that the effect of pressure on this reaction and the changes in kinetics of the reaction must be studied to obtain a clearer sense of the effect. However, previous spot studies have shown the sulfur in  $H_2S$  to poison catalyst sites for CO and stabilize  $Fe_3C$  on the surface, thus deterring its deterioration which has been shown to be an essential part of the deterioration reaction. Generally reactivities for nickel and Inconel seem to increase with increase in  $H_2S$  concentration, although at 500 and 1000 ppm, the temperature differences are also significant to the reactivity. From 600° to 750°C the reactivity of Inconel 600 in 10, 50 and 100 ppm of  $H_2S$  are similar. However, above 815°C reactivity decreases as a function of  $H_2S$ , e.g., 100 ppm, 50 ppm and 10 ppm. This has been verified to be a function of sulfide formation and not metal dusting behavior.

The reactivity of Ni and Inconel 600 at 500 and 1000 ppm of  $H_2S$  is most pronounced. They exhibit a somewhat similar behavior at 500 ppm. The curves

start high, drop almost to zero reactivity (in the case of Inconel, this was accomplished) then rises again in a parabolic form. Inconel 600 at 1000 ppm  $\text{H}_2\text{S}$  experiences an analogous behavior. Ni in 1000 ppm  $\text{H}_2\text{S}$  exhibits the highest reactivity, rising to a maximum at  $750^\circ\text{C}$  then dropping off.

Scanning electron microscopy and x-ray analysis on Ni and Inconel reacted in 50, 100, 500 and 1000 ppm  $\text{H}_2\text{S}$  and in pure CO have revealed the presence of whitest, globular like particles, the increase in size with increasing concentration. These particles have been generally identified as sulphides. Inhibition of metal dusting in nickel base materials using  $\text{H}_2\text{S}$  appears to be highly improbable.

Analysis of the sulfidization at the higher  $\text{H}_2\text{S}$  concentrations indicate the possible temperature dependence of sulfur attack on nickel base materials. This phenomena should be examined further in light of the importance of sulfur in coal gasification systems.



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## APPENDIX I

## Description of Experimental Materials

## Description of carbon monoxide:

Designation - Carbon Monoxide, Matheson Purity

Cylinder - size 1A, 175 scf at 1650 psig.

Purity - 99.99% minimum

Impurities: nitrogen - less than 80 ppm  
methane - less than 15 ppm  
carbon dioxide - less than 10 ppm  
water - less than 5 ppm  
hydrogen - less than 1 ppm  
oxygen - less than 1 ppm

## Description of argon purge gas:

Designation - Argon, Ultra High Purity

Cylinder - size T, 332 scf, 2640 psig.

Purity - 99.999% minimum

## Description of hydrogen sulfide inhibitor gas.

Designation - C. P. Grade

Cylinder - size D, 1307 psig

Purity 99.6%

Impurities: hydrogen sulfide - 99.7%  
carbon disulfide - 0.09%  
carbon dioxide - 0.13%  
methanol mercaptan - 0.02%  
carbonyl sulfide - 0.01%  
sulfur dioxide - 0.05%

## Description of iron wire:

Designation - Marz grade iron

Method of preparation - Electron beam melted and zone refined

Form - 0.020 inch diameter wire, cold formed,  
packed as formed under clean room conditions

Purity - 99.99+% Major impurities include: oxygen - less than 75 ppm  
carbon - less than 15 ppm  
nitrogen - less than 15 ppm  
others - less than 4 ppm each

Description of nickel wire:

Designation - Marz grade nickel

Method of preparation - Electron beam melted and zone refined

Form 0.020" diameter wire cold work to size in clean room conditions

Purity 99.99+% Major impurities include: carbon - 12 ppm max.  
oxygen - 60 ppm max.  
nitrogen - 10 ppm max.

Description of Inconel 600 wire:

Designation - Inconel 600 commercial grade.

Preparation and Purity - Commercial grade.

Form - 0.020" diameter wire - cold formed to size.